Studies on the Detection and Determination of Substances and on the Synthesis of a New Ion Exchanger

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T761

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TABLE OF CONTENTS

LIST OF PUBLICATIONS

1. Allyl Alcohol as a Sensitive and Specific Reagent for the Detection of Mercurous Ions. Anal. Chem. 36, 2040 (1964).

2. Selective Determination of Iron by Potassium cyanide - Potassium Ferrocyanide Reagent. Anal. Chem. 39, 1034 (1967).

LIST OF TABLES

LIST OF FIGURES

A B S T R A C T

Allyl alcohol has been proposed as a new, specific and sensitive reagent for the detection of mercurous ions. The test is simple, rapid and applicable in acidic media. The presence of Ag^+ ions has been found to improve the sensitivity of the test. A mechanism of the reaction has also been tentatively suggested which postulates that mercurous nitrate acts as an oxidizing agent. According to this mechanism mercurous ions are reduced to metallic mercury while allyl alcohol is oxidized to an aldehyde and then to an acid. Some U.V. spectrophotometric studies have also been made in support of the mechanism proposed. Selective detection of unsaturated organic compounds has been achieved using mercurous nitrate as a reagent. The following pairs of substances can be easily differentiated by this method:

(a) acetoacetic ester and malonic ester

(b) α-naphthyl thiourea and other common thiourea derivatives.

(c) formic acid and other organic acids.

(d) allyl alcohol and other allylic alcohols.

A very sensitive method for the spectrophotometric determination of iron has been developed employing the use of potassium cyanide-potassium ferrocyanide reagent. The use of potassium cyanide in the preparation of the reagent is two fold: firstly it inhibits the oxidation of ferrocyanide thus stabilizing the reagent and secondly it masks a large number of common interferences for iron. Other important interferences in the determination have been removed by the use of the masking agents as tartrate, oxalate, citrate, fluoride etc. A comparison of the ferrocyanide and the thiocyanate methods for iron reveals the fact that the former method is more selective and the color developed is more stable than in the latter case.

Studies on the synthesis and properties of a new ion exchanger have been performed. Stannic tungstate has been prepared and its properties such as composition, stability, solubility in different solvents, ion exchange capacity, and pH-titration have been studied in detail. To explore the possibility of some good and important separations, K_d values of metal ions have been determined on this new ion exchanger.

C H A P T E R I

I N T R O D U C T I O N

A number of methods are available for analytically difficult separations.Some of the more important are solvent-extraction, thin layer chromatography, gas chromatography, ion exchange and electrophoresis. Solvent-extraction has received increased attention during the last few years. The more important developments in this field have been the use of computer technique (1), the use of N-benzoyl-N-phenyl hydroxylamine in the determination of zirconium and hafnium (2) and the separation of molybdenum (VI) from rhenium (VI) with pentyl acetate (3). Systematic studies of solvent mixtures for the separation of alkaline earths (4) and for the extraction of zinc oxinate (5) should also be mentioned. However, the largest number of studies have been made in which solvent extraction has been combined with spectrophotometry (6-18).

Chromatography continues to attract attention and some novel techniques have been developed recently.

The separation and identification of group I, II and IV cations by thin layer chromatography on maize-starch is particularly interesting (19, 20). Phosphates have been separated on circular layers of corn-starch (21), while halides and metal-rhodizonates have been separated on silica-gel (22,23). The most significant development in this field is, however, the introduction of molecular-sieve chromatography. In this technique widely different materials such as silica-gel (24), calcium phosphate (25), and the Bio-Gel range of polyacrylamides (26,27) have been used. This technique has, recently, been used for the separation of phosphates (28). Electrophoresis also leads to a number of interesting separations (29,30). Thorium and uranium have been separated as their oxalate complexes (31). Cello-gel strips have combined the advantage of gel and electrophoresis (32) and their use is bound to be exploited in the near future. The use of electrophoretic spectra for the identification of aromatic substances has also considerable novelty (33).

For separations of ions, the ion exchange method is the most efficient. In this method cations may be separated using mixed or complex-forming eluents. Thiocyanate-based eluents are particularly efficient (34).

Liquid ion exchangers have been used to treat silica columns (35) and to use the silica-gel so obtained for thin-layer chromatography (36). The use of synthetic inorganic ion exchangers has not received much attention as this field is still in its infancy. However, by preparing different inorganic ion exchangers and by studying the Kd values of different anions and cations on these ion exchangers a number of useful separations should be possible (37-50).

After separation the ion can be more easily detected or determined. Chalmers and Dick (51) have developed analysis schemes combining solvent-extractions and spectrophotometry. Similarly, circular thin-layer chromatography has been employed (52) for a rapid identification of group I-IV cations after group separation has been affected by classical procedures. Sometimes it is possible to develop methods of detection for inorganic ions and organic substances which do not need any prior separation. For instance spot tests have been developed for silver (53,54), antimony (55-57), thorium (58), mercury(II)(59), arsenic (56,57), tin (56), glyoxal, pyruvic acid, lactic acid (60), copper (61) formanilide, benzoin (62), and zinc (63). The basis of these tests

is either complex formation or ordinary chemical reaction. Therefore, those ions will be difficult to detect, by this procedure, which have weak complex-forming ability. No wonder that few spot tests have been described for non complex-forming ions such as Li^+, Na^+, K^+, Cs^+, Rb^+, and Hg_2^{+2}. It is therefore necessary to spend some effort for developing effective procedures for the detection of these ions.

After the contents of a mixture have been separated and qualitatively detected, the problem of quantitative determination arises. Sometimes separation is achieved from all interfering substances, but more often such a complete separation is not possible. Under these circumstances selective methods of determination have to be developed (64-98). Selectivity is generally achieved by complexing the interfering substances. Only occasionally a reagent is described which reacts specifically with the substance to be determined (99,100). Amongst the ions to be determined Fe^{+3} is one of the most important as it occurs in plant, animals, soils, and alloys. Even though very good methods have been developed (101-109) for the determination of iron, its determination deserves and is receiving considerable attention. And it is worthwhile

to evolve simple procedures which are fast and relatively free from interferences. Existing methods can sometimes be modified (106,110) to increase the selectivity and the sensitivity of the determination.

It was with these objects in view that the present work was undertaken. A new synthetic inorganic ion exchanger has been prepared and the K_d values for various metal ions have been determined. Further studies on this material may lead to better methods of separation of various ionic materials. A new method has been developed for the detection of a non-complexing ion i.e. Hg_2^{+2} ion. This method is specific and sensitive and applicable in common analytical situations. A fast, simple and selective procedure has also been proposed for the determination of iron. The idea is to separate or complex most of the interfering ions before the actual determination is performed. Attempts have also been made to use mercurous nitrate for the selective detection of unsaturated organic compounds. In the following pages are summarized the results, the methods of approach, and the chemistry of the reactions involved for the solution of the problems mentioned above.

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C H A P T E R II

SPECIFIC DETECTION OF MERCUROUS IONS

There are very few reactions which can be used for specific and sensitive detection of mercurous ions. This difficulty results partly from the weak complex forming ability of mercurous ions (1) and partly from the fact that it lacks characteristic color reactions. The mercurous ion disproportionates easily and its detection is based not upon the formation of a new mercurous compound but on the detection of the products of its decomposition i.e. Hg and Hg^{+2} for ascertaining the presence of the parent ion. Since the mercurous ion is easily converted into Hg and HgO by the additions of OH^- ions, the OH^- ions are some times used for the detection of mercurous ions. However, this method has two drawbacks:

(1) It can not be used in acidic media.

(2) It gives rise to the precipitation of numerous metal hydroxides which are likely to interfere in the test.

During paper chromatographic studies of different metal ions in solvents containing allyl alcohol as one of the components it was independently noticed in these laboratories (2) that the spot of mercurous nitrate solution, on exposure to vapours of allyl alcohol, turned black. No other cations gave a black spot under similar conditions. A search of the literature showed that Zappi (3) in 1932 had also noticed the formation of a black precipitate by the action of mercurous nitrate on a number of unsaturated organic compounds. The test appeared to have potentialities for a new, sensitive and specific reaction for the detection of mercurous ions. Therefore, it was decided to investigate the different aspects of this reaction. This chapter summarizes the results of such a study.

E X P E R I M E N T A L

Reagents: Reagent grade or double distilled solvents were used in this study. Allyl alcohol of E. Merck, Darmstadt gave a positive test for aldehyde. It was refluxed over solid potassium carbonate and distilled (4). Mercurous nitrate (E. Merck, Darmstadt) contained some mercuric nitrate. It was therefore dissolved in dilute nitric acid and kept over mercury, when colorless crystals of mercurous nitrate were obtained. The purity of mercurous nitrate was tested by the method of Kolthoff (5). The paper used in the study was Schleicher and Schull 2043a.

Apparatus used: Beckmann Model DU spectrophotometer was used for spectrophotometric studies.

Procedure: To one drop (approximately 0.05 ml) of the slightly acidic test solution is added a drop of 0.1M $AgNO_3$ and a drop of pure allyl alcohol. A black precipitate or coloration shows the presence of mercurous ions. The test

may also be performed by taking a spot (approximately 0.0014 ml) of the test solution on paper followed by a spot of pure allyl alcohol. A black coloration of the spot within 2 minutes shows the presence of mercurous ions.

R E S U L T S

SENSITIVITIES OF THE REACTION OF MERCUROUS ION WITH SOME UNSATURATED ORGANIC COMPOUNDS

In order to find out the best suited reagent for the detection of mercurous ions about 200 organic compounds were tried. Out of these compounds only few unsaturated ones were found to give a black precipitate with mercurous nitrate. Sensitivities of these reagents for the detection of mercurous ions were, therefore, compared.

A drop (approximately 0.05 ml) of the pure liquid was mixed with a drop of mercurous nitrate solutions of different concentrations e.g. 0.1M, 0.01M, 0.001M etc. Ascorbic acid was used in the solid state (1 mg app.) The colors were noted within two minutes. Ammonia was also included for comparison. The results are summarized in table I.

T A B L E I

COMPARISON OF THE SENSITIVITIES OF DIFFERENT ORGANIC COMPOUNDS FOR MERCUROUS IONS ALONG WITH AMMONIA

Compound	Sensitivity (μg)
Allyl alcohol	12.5 (33 on paper)
Acetoacetic ester	50
Acetyl acetone	62.5
Ascorbic acid	25
Ammonia	9 (25 on paper)

Reaction kinetics with the dilution limit of the reagents were also studied to compare their capabilities for mercurous ions.

To a drop (app. 0.05 ml) of 0.1M mercurous nitrate was added a drop of the alcoholic solution of the compound concerned with concentrations varying from 0.001% to 5%. The results are shown in table II.

T A B L E II

COMPARISON OF THE DILUTION LIMITS OF THE REAGENTS FOR MERCUROUS NITRATE

Time (minutes)	Minimum Concentration of the Compound which can give the positive test with Hg_2^{+2}				
	Allyl alcohol	Aceto-acetic ester	Ascorbic acid	Cyan acetic ester	Geraniol
immediately	0.25 %	2.5 %	2.5 %	2.5 %	5 %
1	0.025%	1 %	1 %	1 %	1 %
5	0.025%	1 %	0.25%	1 %	0.25%
10	,,	,,	,,	,,	0.05%
15	,,	,,	,,	,,	,,
20	,,	,,	,,	0.5 %	,,
25	,,	,,	,,	,,	,,
30	,,	,,	,,	0.25%	,,

Acetyl acetone was found ineffective on mercurous nitrate in this range of concentration upto 30 minutes.

Effect of diverse ions on the test:

(a) Cations: A spot of 0.1M solution of the cation concerned was applied to the paper followed by a spot of allyl alcohol. Cu^{+2}, Fe^{+2}, Fe^{+3} were used as sulfates,

As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4} and Ti^{+4} were used as chlorides, while others as nitrates. Mercurous was used as nitrate as well as perchlorate. The results are summarized in table III.

T A B L E III

COMPARISON OF THE REACTION OF ALLYL ALCOHOL AND AMMONIA WITH DIFFERENT CATIONS ON PAPER

Cation	Color with AA	Color with AM	Cation	Color with AA	Color with AM
Ag^{+}	N.C.	Blackish	Ni^{+2}	N.C.	N.C.
Hg_2^{+2} (Nitrate)	B	B	Co^{+2}	,,	L. Blackish
Hg_2^{+2} (perchlorate)	,,	,,	Ba^{+2}	,,	N.C.
Pb^{+2}	N.C.	N.C.	Sr^{+2}	,,	,,
Cu^{+2}	,,	,,	Ca^{+2}	,,	,,
Hg^{+2}	,,	,,	Mg^{+2}	,,	,,
Bi^{+3}	,,	,,	Tl^{+}	,,	,,
Cd^{+2}	,,	,,	UO_2^{+2}	,,	,,
As^{+3}	,,	,,	V^{+5}	,,	B
Sb^{+3}	,,	,,	Be^{+2}	,,	N.C.
Sn^{+2}	,,	,,	Mo^{+6}	,,	D.Br.
Al^{+3}	,,	,,	Ti^{+4}	,,	N.C.

T A B L E III
(Continued)

Cation	Color with AA	Color with AM	Cation	Color with AA	Color with AM
Cr^{+3}	N.C.	N.C.	Th^{+4}	N.C.	N.C.
Fe^{+2}	,,	Brownish	Zr^{+4}	,,	,,
Fe^{+3}	,,	,,	La^{+3}	,,	,,
Mn^{+2}	,,	D.Br.	Ce^{+4}	,,	,,
Zn^{+2}	,,	N.C.	K^{+}	,,	,,
			Na^{+}	,,	,,
			Pd^{+2}	,,	,,

AA = Allyl alcohol B = Black L = Light N.C. = No color

AM = Ammonia Br = Brown D = Dark

(b) Anions: A spot of the solution (0.1M) of the anion concerned was applied to the paper followed by a spot of allyl alcohol. All the anions were used as the sodium salts. No change in color was obtained in any case.

DETECTION OF MERCUROUS ION IN THE PRESENCE OF OTHER CATIONS

The 0.1M solutions of mercurous nitrate and the nitrate of other cations were mixed in specified ratios. One drop of this test solution was mixed with a drop of allyl alcohol (app. 0.05 ml) on a spot plate. The results are summarized in table IV. Ammonia is also included for comparison.

T A B L E IV

SENSITIVITY OF THE ALLYL ALCOHOL REACTION IN PRESENCE OF OTHER CATIONS

Cation present	Allyl alcohol		Ammonia	
	limit of detection (μg)	dilution	limit of detection (μg)	dilution
Ag^{+}	0.008	1:60000	5	1:100
Pb^{+2}	0.5	1:1000	50	1:10
Co^{+2}	0.5	1:10000	50	1:10
Cr^{+3}	0.5	1:1000	500	1:1
Bi^{+3}	0.5	1:1000	50	1:10

A mixture was also prepared by taking 0.1 ml of the 0.1M solutions of nitrates of each of the following cations: Ag^{+}, Hg_2^{+2}, Pb^{+2}, Bi^{+3}, Cd^{+2}, Co^{+2}, Cr^{+3}, Ba^{+2}, Fe^{+3}. A drop of this test solution was mixed with a drop of allyl alcohol. An immediate black coloration was obtained showing the presence of Hg_2^{+2}.

Comparative study of the interference by anions in the Allyl Alcohol and ammonia tests for mercurous ions:

A drop (app. 0.05 ml) of 0.1M $Hg_2(NO_3)_2$ solution was mixed with a drop of 0.1M solution of the anion concerned in the form of sodium salt followed by a drop of allyl alcohol or liquor ammonia as required. The results are summarized in table V.

T A B L E V

EFFECT OF ANIONS ON THE $[Hg_2(NO_3)_2$ - ALLYL ALCOHOL$]$ REACTION

Anion	Test with allyl alcohol	Test with ammonia
Acetate	Positive	Positive
Bromate	Positive	Positive
Bromide	Positive	Positive

T A B L E V
(Continued)

Anion	Test with allyl alcohol	Test with ammonia
Carbonate	Positive	Positive
Chloride	Positive	Positive
Fluoride	Positive	Positive
Iodide	Negative	Positive
Nitrate	Positive	Positive
Nitrite	Positive	Positive
Phosphate	Negative	Positive
Oxalate	Positive	Positive
Silicate	Positive	Positive
Sulfate	Positive	Positive
Sulfite	Positive	Positive

U.V. Spectrophotometric Studies:

(a) Absorption spectrum of allyl alcohol: The absorption spectrum of 0.01% (V/V) aqueous solution of allyl alcohol against distilled water is shown in figure 1, curve 1.

(b) Absorption spectrum of Mercurous nitrate: An absorption spectrum of mercurous nitrate (10^{-4}M in distilled water) against distilled water is given in figure 1, curve 2.

(c) Absorption spectrum of Sodium chloride:

Figure 1, curve 3 shows the absorption spectrum of sodium chloride (5×10^{-4}M) against distilled water.

(d) Absorption spectrum of allyl alcohol - mercurous nitrate reaction product: To one milliliter of allyl alcohol were added 10 ml of 0.1M mercurous nitrate solution. It was filtered after 5 minutes and to the filtrate were added 10 ml of 0.5M NaCl (aqueous) to precipitate out any mercurous ions left unreacted. After filtering the filtrate was diluted to 100 ml with distilled water. The spectrum of this solution after further diluting 100 times is shown in figure 1, curve 4.

(e) Absorption spectrum of allyl alcohol - Sodium nitrate mixture:

The absorption spectrum was taken after replacing mercurous nitrate in the procedure (d) with $NaNO_3$. The result is summarized in figure 1, curve 5.

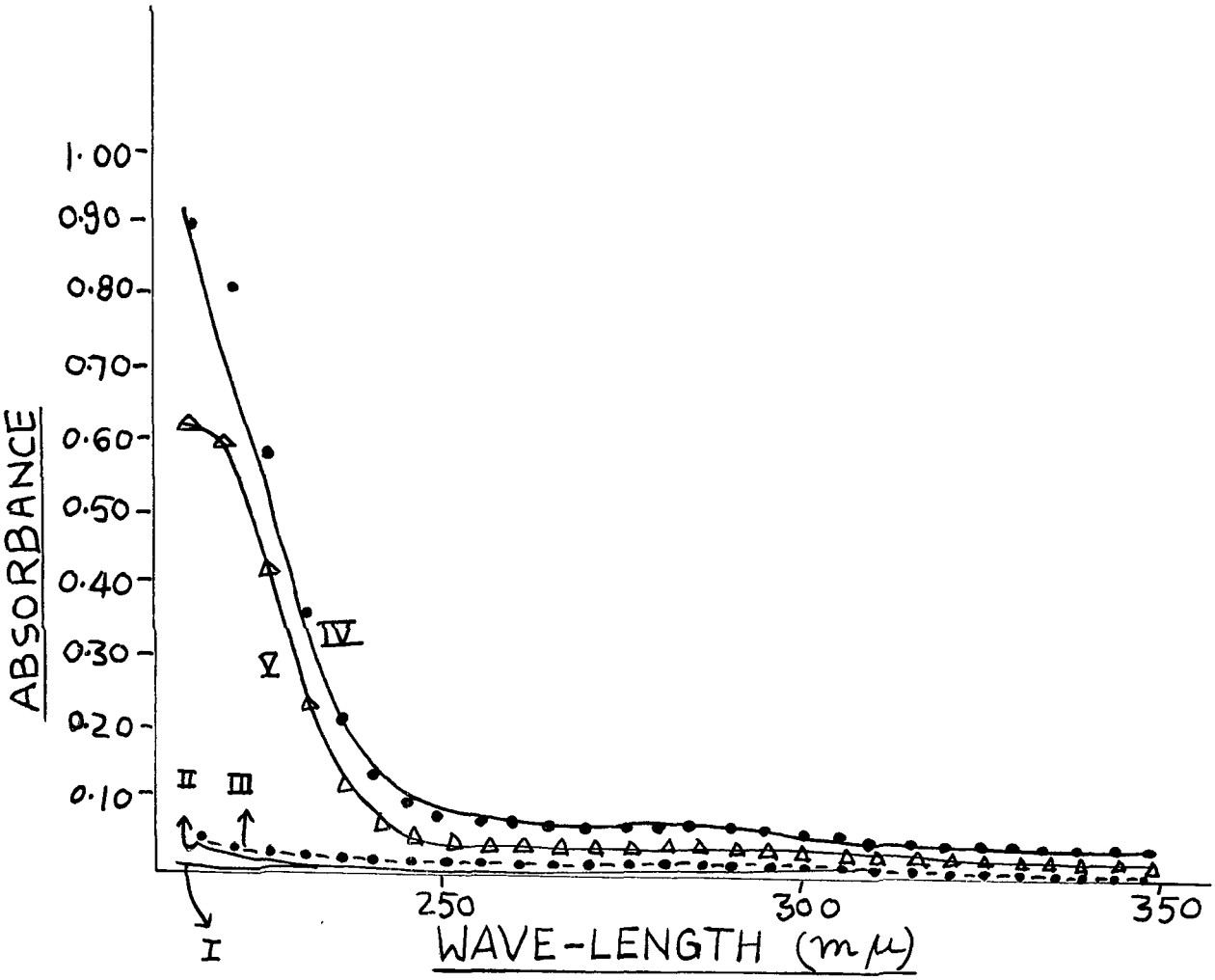

FIGURE - 1. U.V. ABSORPTION SPECTRA OF:

(i) ALLYL ALCOHOL
(ii) MERCUROUS NITRATE
(iii) SODIUM CHLORIDE
(iv) MERCUROUS NITRATE-ALLYL ALCOHOL MIXTURE
(v) SODIUM NITRATE-ALLYL ALCOHOL MIXTURE

M E C H A N I S M

When mercurous nitrate was treated with allyl alcohol a black precipitate was obtained. This precipitate gave a negative test for carbon and nitrogen. On heating strongly a droplet of mercury was left on the spatula. Later on it was noticed that even without heating the black precipitate gave droplets of mercury on standing. It is therefore clear that the black precipitate consists of pure mercury.

There are now two possibilities:

(i) Mercurous nitrate oxidizes allyl alcohol first to an aldehyde and then to an acid (Equation 1).

(ii) Mercurous nitrate is decomposed catalytically by allyl alcohol according to equation 2.

$$Hg_2^{+2} + CH_2 = CH-CH_2OH \longrightarrow 2Hg + 2H^+ + CH_2 = CH-CHO$$

$$Hg_2^{+2} + CH_2=CH-CHO + H_2O \longrightarrow 2Hg + 2H^+ + CH_2=CH-C\begin{matrix}=O\\ -OH\end{matrix} \quad \ldots (1)$$

$$Hg_2(NO_3)_2 \longrightarrow Hg + Hg(NO_3)_2 \ldots\ldots\ldots (2)$$

The mechanism given in equation (2) has been suggested by Zappi and Manini (6). However, our observations do not entirely agree with this point of view.

Test for aldehyde in the products of reaction:

The product of reaction of mercurous nitrate with allyl alcohol was treated with excess of sodium chloride to remove any unreacted mercurous. Mercurous chloride was filtered off and a test for aldehyde was performed with (a) Nitroprusside reagent (b) 2,4-dinitrophenyl hydrazine and (c) Schiff's reagent. In each case a negative test was obtained. This shows that no aldehyde is formed in this reaction.

Test for acid in the products of reaction:

One milliliter of pure allyl alcohol was titrated with $\frac{N}{107}$ sodium hydroxide solution using phenolphthalein as an indicator and a pink color was obtained with only one drop of the alkali. Ten milliliters of aqueous saturated mercurous nitrate (7) was then treated with excess sodium chloride and filtered. The filtrate, on titration, required 6.9 ml of sodium hydroxide for complete

neutralization. One ml of allyl alcohol was then treated with 10 ml of the aqueous saturated mercurous nitrate used earlier. The precipitate (mercury) was allowed to settle and filtered. The filtrate now required 36.1 ml of sodium hydroxide for neutralization. This shows conclusively that some acid is produced in this reaction. The same results were consistently obtained when the procedure was repeated. Thus when mercurous nitrate is added to allyl alcohol a larger amount of alkali is needed for neutralization than the alkali required to neutralize allyl alcohol and mercurous nitrate separately. This can not be explained on the assumption that in the presence of allyl alcohol mercurous ions disproportionate into mercury and mercuric ions. Further, when we replaced mercurous nitrate with mercuric nitrate we found that the allyl alcohol-mercuric nitrate mixture did not require more alkali than its components. This, therefore, confirms the mechanism of the reaction proposed by us. We have also tried to explore this mechanism with the help of U.V. spectrophotometry (see figure 1). It is quite clear from the figure that mercurous nitrate and allyl alcohol as such do not appreciably absorb in the region studied while the product of allyl alcohol-mercurous nitrate reaction absorbs strongly

in the region below 220 mμ . This, however, is also the region where nitrate itself absorbs strongly (8). To see the effect of nitrate on the reaction, mercurous nitrate was replaced by sodium nitrate, and the spectrum of allyl alcohol-sodium nitrate mixture (figure 1, curve 5) was drawn. Although the absorbance of this mixture below 220 mμ is high, a critical study of the curves clearly shows that the reaction product with mercurous nitrate absorbs more strongly than that with sodium nitrate. The results were found reproducible when excess of mercurous ions was removed by passing the reaction mixture through a cation exchange resin in Na-form, instead of using sodium chloride to minimize the presence of other unnecessary ions in the reaction mixture. This high absorbance below 220 mμ is, therefore, due to the presence of a conjugated double bond system.

D I S C U S S I O N

Allyl alcohol offers a sensitive and specific test for the detection of mercurous ions without changing the pH of the solution significantly. Since this reaction is given both by mercurous nitrate and perchlorate, it is clear that the reaction is not due to the anions. The studies indicate that this test is superior to ammonia in many aspects. In the presence of other cations which is generally the case in ordinary analysis allyl alcohol is a more sensitive and reliable reagent than ammonia (table IV). The presence of other cations probably increases the sensitivity of the reaction because these metal ions act as promoters in the reduction of mercurous ions to mercury. However, this test is slightly less sensitive when we have to test for pure mercurous solutions (table I). The interference by other cations is almost negligible with the allyl alcohol test. Ammonia, on the other hand, produces colored precipitates with a large number of cations (table III). The effect of anions on the allyl alcohol and ammonia tests is interesting (table V). Positive tests are obtained in

the presence of almost all common anions. The presence of iodide and phosphate interferes with the allyl alcohol test. This is possible because in the neutral medium mercurous iodide and mercurous phosphate are not sufficiently ionized to produce enough mercurous ions for reduction. Since the stability of mercurous iodide and phosphate is low in alkaline medium, a positive test for mercurous ions is obtained with ammonia even in the presence of phosphate and iodide. This interference can, however, be removed by complexing agents such as $AgNO_3$ and $Zr(NO_3)_4$. If iodide is present, it can be removed by first treating the test solution with $AgNO_3$ and filtering out the resulting yellow precipitates of silver iodide. If phosphate is present in the solution, then zirconium nitrate is added to precipitate out zirconium phosphate. In the filtrate the test for mercurous ions is carried out. Thus, allyl alcohol can be used with advantage in testing for mercurous ions in the neutral and acidic media. Here, the ammonia test is not suitable for obvious reasons.

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C H A P T E R III

DETECTION OF UNSATURATED ORGANIC COMPOUNDS

In order to find the most sensitive reagent for the detection of mercurous ions a number of unsaturated organic compounds were tried (table I). As a result of this study it became apparent that the test for mercurous ions could be reversed and mercurous nitrate could be used for the detection of unsaturated organic compounds. Zappi and coworkers (1,2) in a series of papers, first suggested the use of mercurous nitrate as a general reagent for the detection of allylic bodies and unsaturated organic compounds. The test, however, was never extensively used owing to its lack of selectivity. The necessity for such a test is enhanced by the fact that tetranitromethane, which is a general reagent for unsaturated organic compounds, gives a negative response with allylic bodies and α,β - acids, esters, aldehydes and ketones (3). It was, therefore, decided to explore the possibility of devising a method for the selective detection of unsaturated organic compounds using the reaction with mercurous nitrate. As

a result, it was found that it is possible to modify the conditions of reaction in such a manner as to make mercurous nitrate a selective reagent for the detection of these compounds. This chapter summarizes the results of such an approach. The papers impregnated with mercurous nitrate were also used for this purpose.

and to the centrifugate are added a few drops of 4N HNO_3 to make it distinctly acidic. Then a few drops of app. 0.1M mercurous nitrate solution are added to the solution. A black color or precipitate shows the positive response.

(3) Test on paper: Paper strips are impregnated with approximately 0.1M mercurous nitrate solution. The paper is dried in air at room temperature. A capillary spot of the pure organic compound to be tested is placed on this paper. The color is observed after 5 minutes. A black to brown color of the spot shows the positive response. Test is also done on elevated temperature by keeping the paper for 30 minutes at $60^{o}C$. Solid compounds are taken as a saturated solution in ethanol.

R E S U L T S

A. STUDIES IN SOLUTIONS

1. In the absence of thioureas: In the table VI, given below, compounds are shown which give positive response with mercurous nitrate. The reaction was studied with time.

T A B L E VI

COMPOUNDS GIVING A POSITIVE RESPONSE WITH MERCUROUS NITRATE

Compounds	Time
Allyl alcohol	immediately
Cinnamyl alcohol	30 minutes
Geraniol	1 minute
Farnesol	5 minutes
Crotonaldehyde	15 minutes
Acetyl acetone	1 minute
Ascorbic acid	immediately
Acetoacetic ester	immediately
Cyanacetic ester	5 minutes

The following organic compounds did not show a positive response even in 60 minutes:

ALCOHOLS: Methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, amyl, tert-amyl, octyl, benzyl and cyclohexanyl alcohols, geraniol, ethylene glycol and propylene glycol.

ALDEHYDES: Formaldehyde, acetaldehyde, benzaldehyde, chloral, salicylaldehyde, resorcylaldehyde and o-nitrobenzaldehyde.

KETONES: Methyl ethyl, methyl n-propyl and methyl isopropyl ketones, acetone, acetonyl acetone, acetophenone, cyclohexanone, anthraquinone and α-amino anthraquinone.

ACIDS: Formic, acetic, propionic, butyric, Oxalic, tartaric, citric, mucic, cinnamic, lauric, myristic, camphoric, stearic, m-nitrobenzoic, benzoic, salicylic and phthallic acids.

ESTERS: Methyl, ethyl, amyl, and mono-bromo ethyl acetates; ethyl, amyl, and ethyl p-amino benzoates, ethyl formate,

diethyl oxalate, ethyl acetone dicarboxylate, diethyl malonate, dimethyl sulfate, and ethyl nitrate.

AMINES AND AMIDES: Methyl, diethyl, and diphenyl amines; dimethyl, diethyl, and chloro anilines; pyridine, benzidine, p-anisidine, acridine; formamide, acetamide and urea.

CARBOHYDRATES: D-glucose, fructose, lactose, dextrin, and raffinose.

ANHYDRIDES AND ACID CHLORIDES: Acetic anhydride, and benzyl chloride.

HYDROCARBONS AND SUBSTITUTED HYDROCARBONS: Hexane, toluene, cyclohexane, nitrobenzene, chloroform, tetrahydrofuran, carbon tetrachloride, carbon disulfide, arsenobenzene, acenaphthene, anthracene.

PHENOLS: Phenol, amide phenol, p-amido phenol, amido phenol p-chlorohydrate, α-naphthol, β-naphthol, decahydro transbeta naphthol, pyrogallol, resorcinol, catechol, and pyrocatechol.

MISCELLANEOUS: α-nitro-naphthalene, diacetyl, azobenzol, caffeine, kerosol, casein, congo red, 2:4 dinitrophenyl hydrazine, diphenyl carbazide, dimethyl glyoxime, borneol, ethylene bromide, phenolphthalein, ethylene dibromide, ethylene urethane, alizarin-S, cholesterol, and methylal.

B. STUDIES ON PAPERS IMPREGNATED WITH MERCUROUS NITRATE

Impregnated papers with mercurous nitrate were also used for the detection of unsaturated organic compounds. The results are summarized below:

1. Compounds giving positive response at room temperature and at 60°C.

   Alcohols: Allyl alcohol

   Amines: Diethyl, monoethanol, and diethanol amines.

   Acids: Ascorbic acid.

   Thioureas: Allyl, diphenyl, O-tolyl, and sym-isopropyl thioureas; thiourea.

2. Compounds giving negative response at room temperature but positive response at elevated temperature:

Alcohols: Geraniol

Acids: Formic acid.

Aldehydes: Formaldehyde (10 minutes) and acetaldehyde.

Amines: Diethyl aniline

Esters: Ethyl formate and ethyl acetoacetate.

3. Compounds giving negative response both at room temperature and elevated temperature:

Alcohols: Methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, tert-butyl, amyl, tert-amyl, octyl, cinnamyl, and cyclohexanyl alcohols; ethylene glycol, propylene glycol, and glycerine.

Aldehydes: Formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde, chloral,

salicylaldehyde, vanillin, nitrobenzaldehyde, and trithio-formaldehyde.

Acids: Acetic, propionic, butyric, oxalic, tartaric, citric, capric, mucic, cinnamic, lauric, myristic, camphoric, stearic, benzoic, salicylic, phthallic and nitrobenzoic acids.

Esters: Methyl, ethyl, and monobromo ethyl acetates; ethyl and diethyl malonates; ethyl formate and diethyl oxalate.

Ketones: Methyl ethyl and methyl n-propyl ketones; acetone, acetonyl acetone, and benzophenone.

Amines: Ethyl aniline, rosaniline, triethanol amine, and o-tolidine.

Thioureas: α-naphthyl thiourea.

D I S C U S S I O N

Two basic modifications made in Zappi's method for the detection of unsaturated organic compounds are as follows:

a. Lowering of pH and

b. Lowering of temperature.

When the reaction is performed in acidic medium substances like amines do not give a positive reaction with mercurous nitrate. If the reaction is performed at room temperature a large number of organic compounds do not give this test. The only interference remains from thioureas which give a positive test even at low temperature and low pH. Therefore, the interference from these compounds is removed by complex formation with mercuric nitrate. If thioureas are precipitated by the addition of mercuric nitrate the reaction becomes fairly selective. The effect of time on the reaction was also studied. It was found that of the allylic alcohols tested the simple allyl alcohol gives a positive test immediately while the substituted alcohols take a little more time. It is thus possible

to distinguish between the allylic alcohols as a result of this reaction. This reaction is also useful in distinguishing between malonic ester and acetoacetic ester. Thus using a 5% alcoholic solution no test is obtained with malonic ester while a fairly positive response is obtained from acetoacetic ester. This may be explained on the assumption that it is the enolic form of the ester which reacts with the mercurous ions. However since malonic ester exists mostly in the ketonic state hence it does not give a positive response. Acetoacetic ester, on the other hand, exists in enolic form to a much greater extent (7%) and hence gives a positive test. Of the common acids tried only ascorbic acid gave a positive response. Therefore, this method can be used for the selective detection of ascorbic acid also. Ascorbic acid can be considered as an unsaturated alcohol and its positive response with mercurous nitrate can therefore be easily explained.Mercurous nitrate paper also offers interesting possibilities. Thus if a substance does not contain N and S and gives a positive response with mercurous nitrate paper it shows the possibility of allyl alcohol and ascorbic acid. Similarly it is possible to distinguish α-naphthyl thiourea from other common thiourea derivatives since it gives a negative test

both at ordinary temperature and at 60°C. Formic acid is the only acid which gives a positive response at 60°C and no response at ordinary temperature. This method can therefore be used for the detection of formic acid in other acids.

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C H A P T E R IV

SELECTIVE DETERMINATION OF IRON

Iron is an important constituent of soil, plants, animals and alloys, and therefore its detection and determination has attracted considerable attention. A number of useful methods for the spectrophotometry of iron have been developed (1). The simplest method for the determination of iron is probably the thiocyanate method while the method based on phenanthroline is, at present, the most selective. Recently (2) an effort was made to reduce the number of interferences in the phenanthroline-method and in this manner to improve the utility of the method. Ferrocyanide had also been proposed earlier as a reagent for the determination of iron (3,4). Walker (5) had compared the thiocyanate and ferrocyanide methods for the colorimetric determination of small amounts of iron and found that both methods are not applicable in the presence of oxalates and fluorides, and boiling for a short time was recommended in the ferrocyanide method. Baba in 1941 used potassium

ferrocyanide for determining ferric iron colorimetrically(4) and found that the results obtained were lower than the gravimetric method, the difference being 8.4% and ammonium sulfate interfered. An effort was therefore made to develop a fast and selective procedure for the determination of Fe(III) utilizing ferrocyanide as a reagent. The present chapter deals with such a procedure.

E X P E R I M E N T A L

Reagents: All the reagents and chemicals used in the study were either E. Merck(Darmstadt, Germany) grade or B.D.H. Analar.

A standard iron solution containing 1000 ppm Fe was prepared from B.D.H. Analar ferric ammonium sulfate in 1% V/V sulfuric acid.

The potassium cyanide-potassium ferrocyanide reagent consisted of a 1:1:1 mixture of aqueous 5% potassium cyanide, 5% potassium ferrocyanide in 0.2% aqueous sodium carbonate, and glacial acetic acid.

A buffer solution of pH 1.42 was prepared by adding 200 ml of 1N sodium acetate to 240 ml of 1N HCl and diluting to 1 liter.

Apparatus used: All the spectrophotometric studies were performed on a Bausch and Lomb spectronic 20 colorimeter. pH- measurements were made on Philips pH-meter.

Procedure:

A. In absence of Impurities: To the solution containing 5-50 μg of Fe(III) in 1% H_2SO_4, are added 0.2 ml of 5% KCN, 0.2 ml of the coloring reagent and 5 ml of buffer. With distilled water the volume is made upto 10 ml and the absorbance is measured at 710 mμ.

B. In presence of Ba, Sr, and Hg(I): If a precipitate appears after the addition of KCN, it is centrifuged off and to the centrifugate are added 0.2 ml of 5% KCN, 0.2 ml of the reagent and 5 ml of buffer. After diluting to 10 ml the absorbance of the solution is measured at 710 mμ.

C. In the presence of Th(IV) and Y(III): To the solution in 1% H_2SO_4, sodium fluoride solution is added containing about 2000 μg fluoride and rest of the procedure is the same as above.

D. In the presence of NO_2^- and Tl(I): If NO_2^- is present the mixture is heated with 1% H_2SO_4 for 15 minutes before adding KCN. After cooling all other reagents are added as in the above procedures and the absorbance is measured at 710 mμ as usual.

E. In the presence of Zr(IV) and Sb(III): If the test solution contains Zr(IV) as impurity, it is masked by adding sodium tartrate (2000 μg tartrate). The usual procedure is followed. When Sb(III) is taken as potassium antimonyl tartrate it does not interfere in the procedure.

R E S U L T S

1. Absorption Spectrum of the blue color:

The absorption spectrum of the color produced in the procedure was measured against the blank and the results are shown in the figure 2. The wave length of maximum color absorbance is 710 mμ.

2. Effect of time on the absorbance:

The blue color was produced with iron (III) and reagent as in the procedure. The absorbance of this color was measured at time intervals. The results are given in figure 3. There was no change in absorbance for 5 hours against the blank.

3. Effect of temperature on the absorbance:

The temperature of the blue color produced in the procedure was raised from room temperature to 80°C and the absorbance was measured after each rise in the temperature. Figure-4 summarizes the results. There is no effect due to

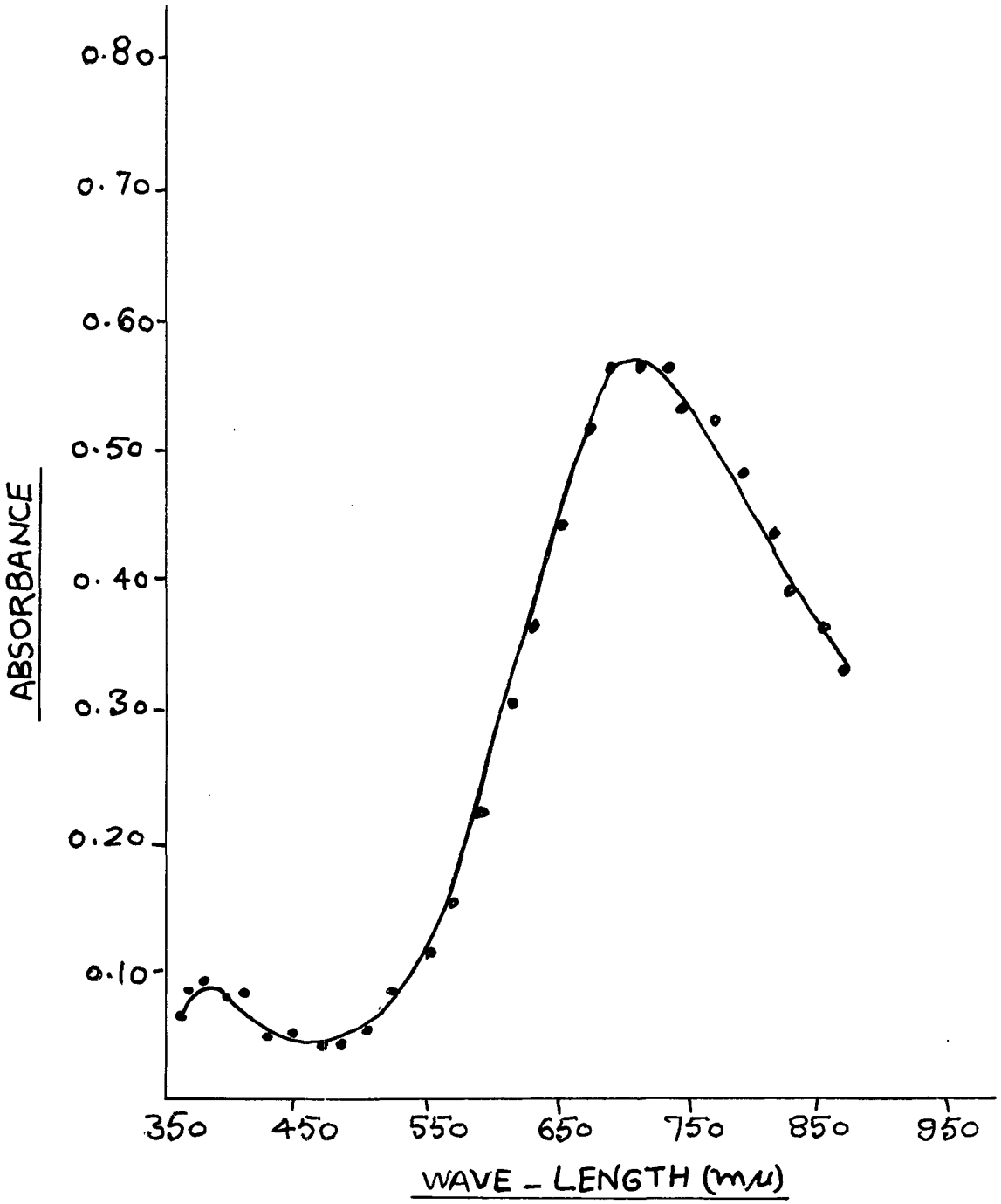

FIGURE - 2. ABSORPTION SPECTRUM OF $[Fe^{+3}$-KCN-$K_4Fe(CN)_6]$ COLOR.

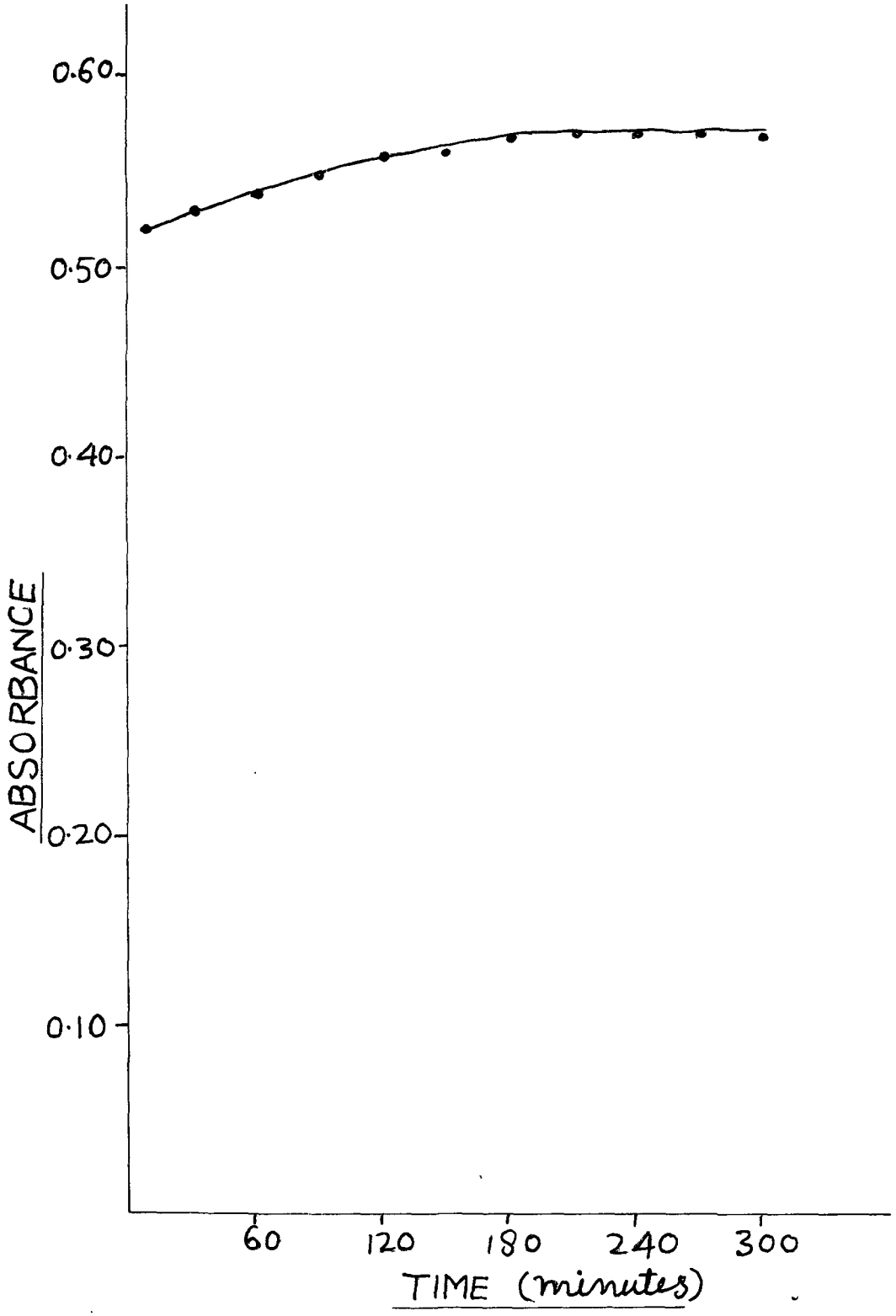

FIGURE - 3. EFFECT OF TIME ON THE ABSORBANCE OF $[Fe^{+3}-KCN-K_4Fe(CN)_6]$ COLOR.

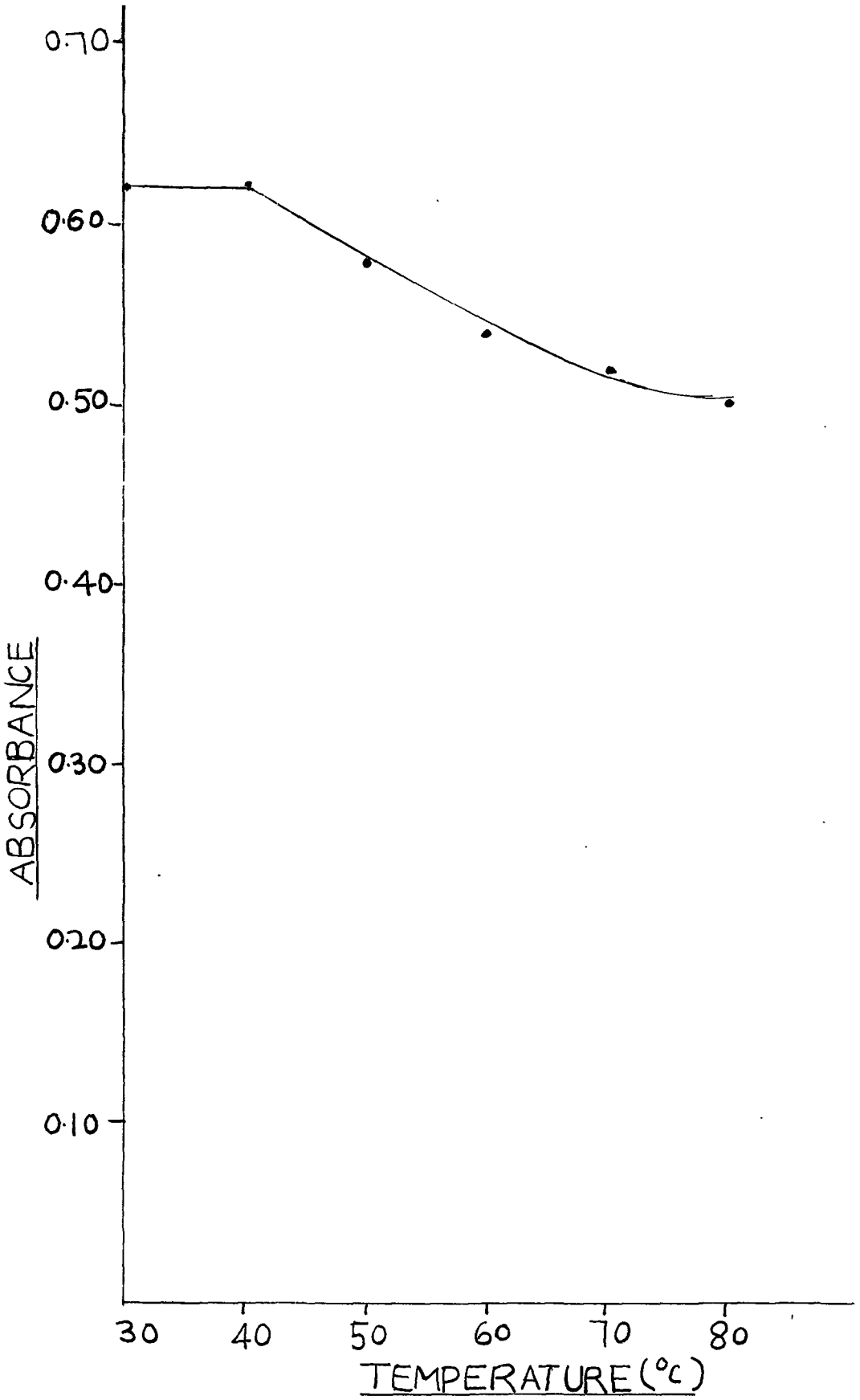

FIGURE - 4. EFFECT OF TEMPERATURE ON THE ABSORBANCE OF $[Fe^{+3}\text{-}KCN\text{-}K_4Fe(CN)_6]$ COLOR.

temperature upto 40°C and then there is a decrease of about 0.025 absorbance units per 10°C upto 80°C.

4. Effect of pH on the absorbance:

To see the effect of pH on the blue color absorbance was measured at different pH values. The pH was raised by adding a saturated solution of sodium bicarbonate dropwise to the solution. The results are shown in figure 5.

5. Effect of excess KCN on the color intensity:

The blue color was produced in the presence of different volumes of KCN solution following the general procedure and the absorbance was measured in each case. The color intensity of the solution decreases with the increase in the amount of KCN as shown in the figure 6.

6. Effect of excess reagent on the color intensity.

The procedure of the color development was repeated with different volumes of the reagent and the absorbances of the colors in all cases were measured at 710 mμ. Excess of reagent has no effect on the intensity of the color as is evident from the figure 7.

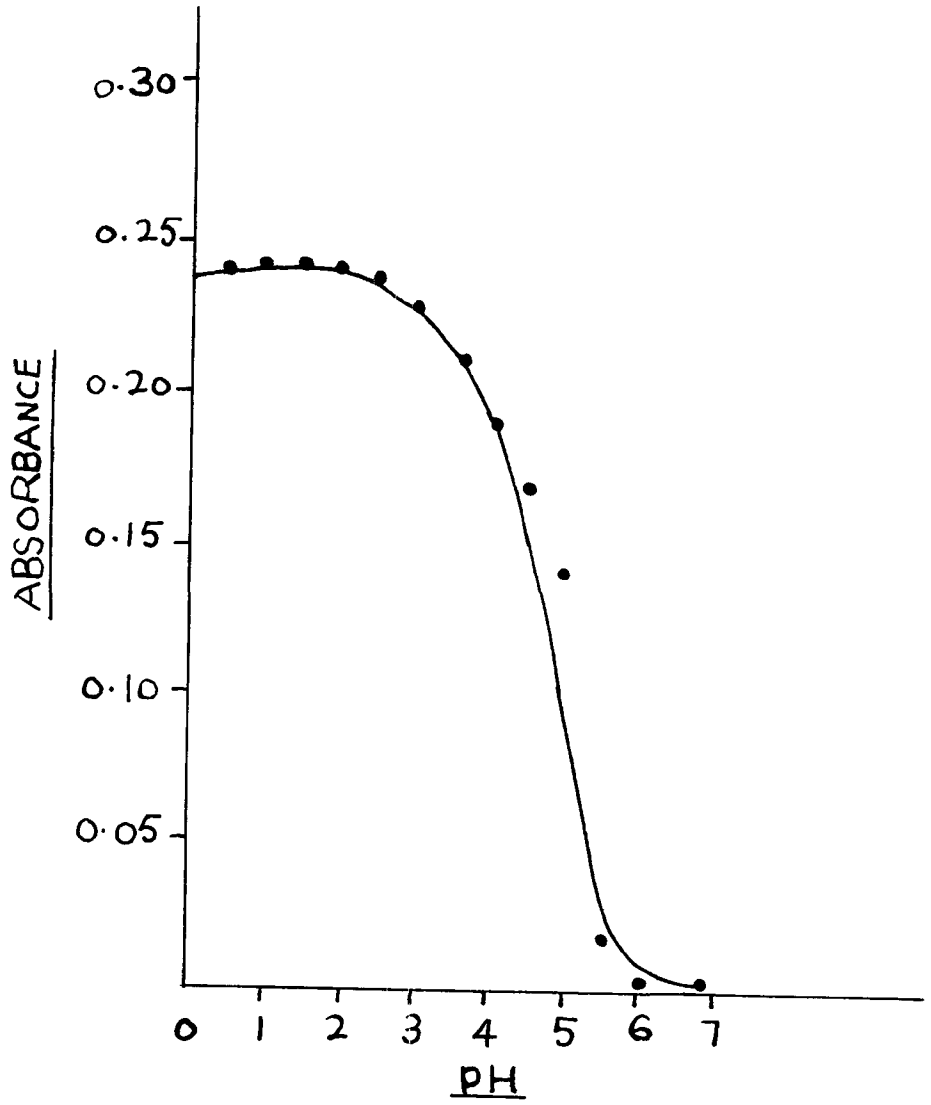

FIGURE - 5. EFFECT OF pH ON THE ABSORBANCE OF $[Fe^{+3}$-KCN-$K_4Fe(CN)_6]$ COLOR.

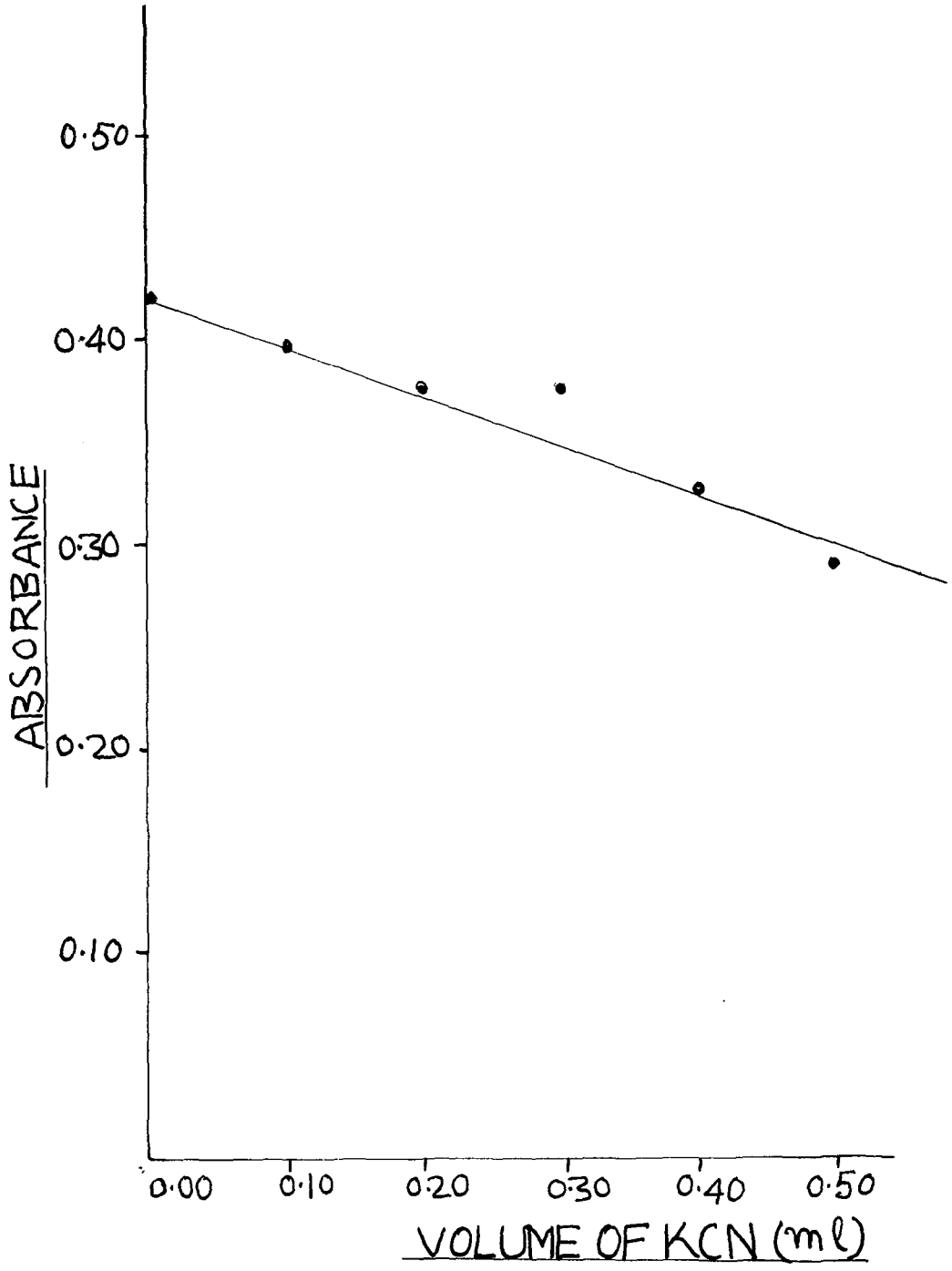

FIGURE - 6. EFFECT OF EXCESS KCN ON THE ABSORBANCE OF $[Fe^{+3}\text{-}KCN\text{-}K_4Fe(CN)_6]$ COLOR.

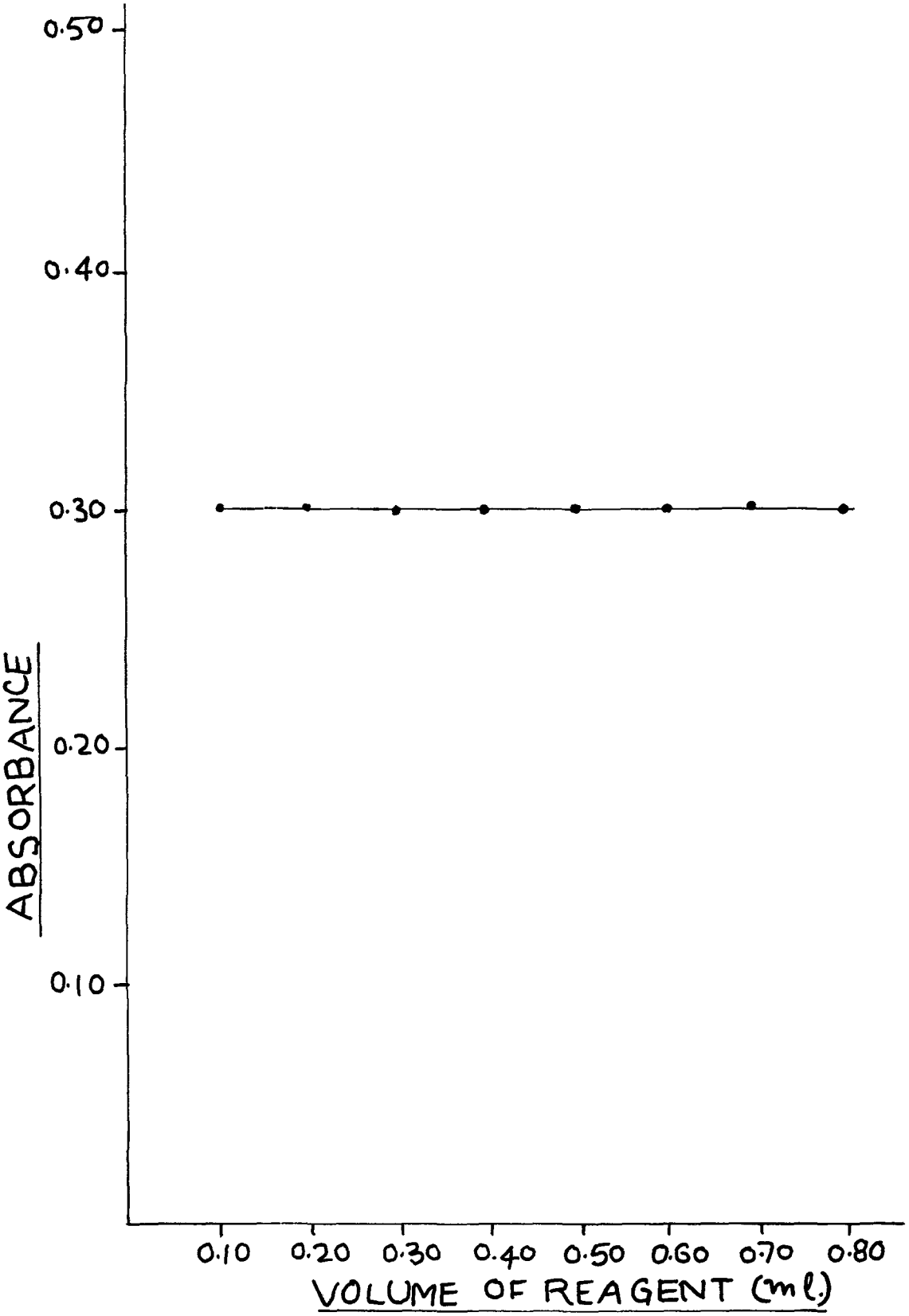

FIGURE - 7. EFFECT OF EXCESS REAGENT ON THE ABSORBANCE OF $[Fe^{+3}\text{-}KCN\text{-}K_4Fe(CN)_6]$ COLOR.

7. Calibration curve for iron:

Taking different amounts of Fe(III) (5 to 50 μg) blue colors were developed using the procedure listed above. Absorbances of these solutions were measured at 710 mμ and it was found that they were directly proportional to the concentration of Fe(III) and followed the Beer-Lambert law strictly. Absorbance for 5 μg Fe(III) was 0.077 while for 50 μg it was 0.71 the standard deviations being 0.0025 and 0.005 respectively (Figure 8).

8. Effect of diverse ions:

A. Cations: More than 30 common cations were studied to see their effect on the determination of Fe(III). Using the general procedure adopted, many cations were found to be tolerable even at 100-fold concentration to Fe(III), some at and above 5-fold and others at only 1-fold. The results are summarized in tables VII - IX.

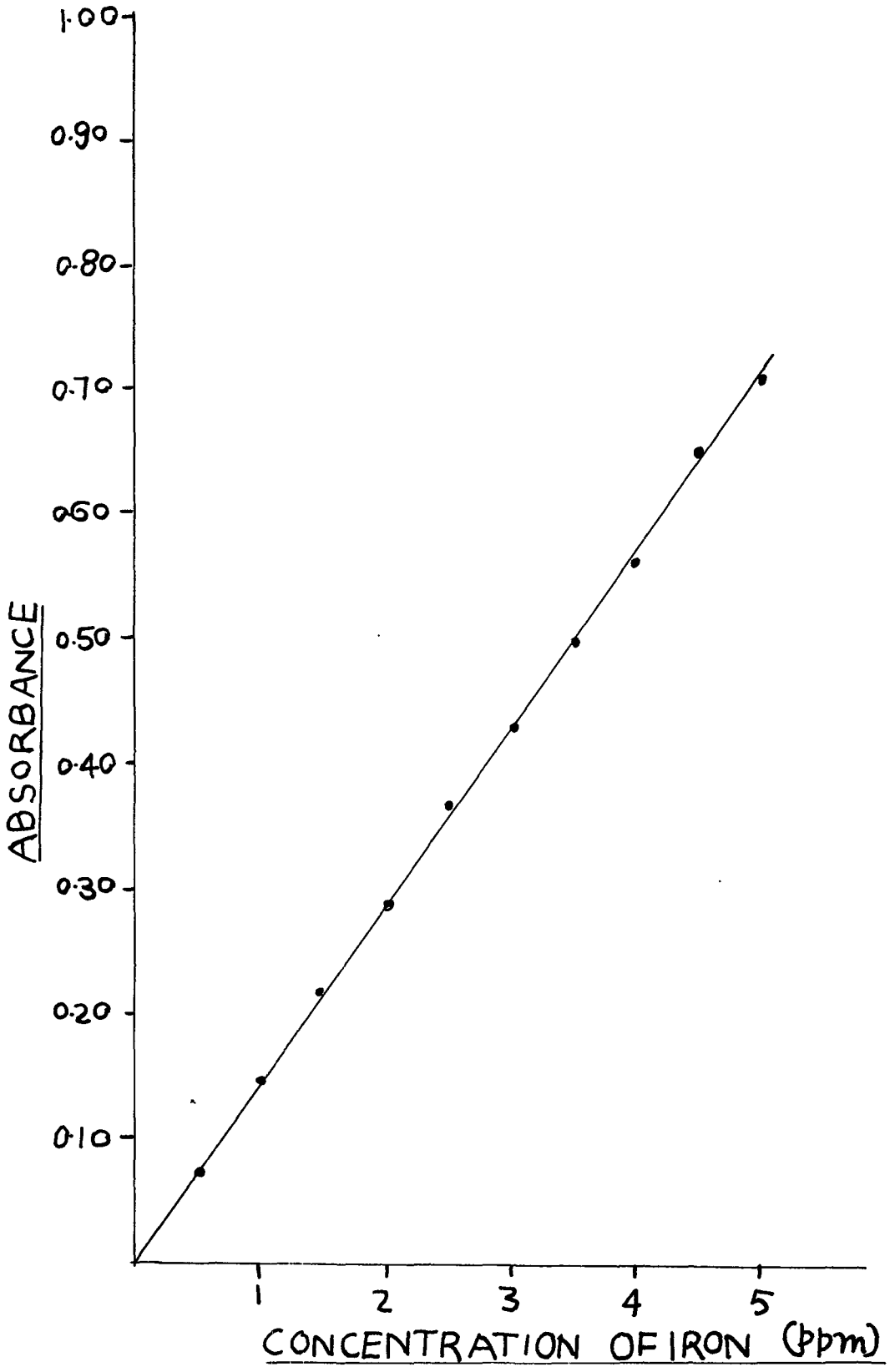

FIGURE - 8. CALIBRATION CURVE FOR IRON.

T A B L E VII

CATIONS WHICH DO NOT INTERFERE

Cation present (μg)		Fe(III) taken (μg)	Fe(III) found (μg)	% error
2080	Cr^{+3}	20	20	0.00
2000	Pt^{+6}	,,	21	+ 5.00
2241.8	Se^{+6}	,,	19.75	- 1.25
2000	Mg^{+2}	,,	20	0.00
12761	Te^{+6}	,,	20.5	+ 2.50
2698	Al^{+3}	,,	20.5	+ 2.50
2000	Ca^{+2}	,,	20.75	+ 3.75
1376.6	Ba^{+2}	,,	20	0.00
2000	Sr^{+2}	,,	20.5	+ 2.50
10030	Hg^{+}	,,	21	+ 5.00
2320	Th^{+4}	,,	20.5	+ 2.50
10360	Pb^{+2}	,,	21	+ 5.00
2030	Sb^{+3}	,,	20	0.00
18386	W^{+6}	,,	20	+ 0.00
1064	Pd^{+2}	,,	20.75	+ 3.75
2030	Zr^{+4}	,,	20.5	+ 2.50
2320	Tl^{+}	,,	20	0.00

T A B L E VIII

CATIONS WHICH ARE TOLERABLE AT AND ABOVE 5-FOLD CONCENTRATION OF Fe(III)

Cation present (μg)		Fe(III) taken (μg)	Fe(III) found (μg)	% error
903	Be^{+2}	.20	21	+ 5.00
147.4	Sn^{+2}	,,	21	+ 5.00
294.8	Sn^{+4}	,,	20	0.00
209	Bi^{+3}	,,	21	+ 5.00
250	U^{+6}	,,	19.5	- 2.50
252	Ti^{+4}	,,	19.75	- 1.25
749.1	As^{+3}	,,	20.75	+ 3.75
120	Mo^{+6}	,,	21	+ 5.00
147.3	Co^{+2}	,,	21	+ 5.00
127.5	V^{+4}	,,	20.5	+ 2.50

T A B L E IX

CATION WHICH ARE TOLERABLE AT EQUAL CONCENTRATIONS OF Fe(III)

Cation present (μg)		Fe(III) taken (μg)	Fe(III) found (μg)	% error
27.5	Mn^{+2}	20	20	0.00
25	Ni^{+2}	,,	20	0.00
63.54	Cu^{+2}	,,	21	+ 5.00
21.8	Ag^{+}	,,	20	0.00
24.9	Os	,,	20	0.00

B. Anions: To the Fe(III) solution the anion under study was added and then Fe(III) was determined according to the procedure. Out of about 20 anions studied, most were found non interfering in the determination of Fe(III) even at 100-fold concentrations. The results are summarized in table X.

T A B L E X

ANIONS TOLERABLE AT 100-FOLD CONCENTRATION OF Fe(III)

Anion present (μg)		Fe(III) taken (μg)	Fe(III) found (μg)	% error
2250	Formate	20	20	0.00
2540	Iodide	,,	20	0.00
2000	Bromide	,,	20.5	+ 2.50
2080	Citrate	,,	21	+ 5.00
2087.5	Chlorate	,,	20	0.00
2200	Oxalate	,,	20	0.00
2050	Iodate	,,	20.5	+ 2.50
2560	Bromate	,,	20.5	+ 2.50
2317	Arsenate	,,	20.25	+ 1.25
5940	Arsenite	,,	21	+ 5.00
2000	Nitrite	,,	21	+ 5.00
2000	Tartrate	,,	21	+ 5.00
2000	Sulfite	,,	20	0.00
2090	Fluoride	,,	20.25	+ 1.25
2376	Phosphate	,,	20.25	+ 1.25
2380	Hydrogen phosphate	,,	20.25	+ 1.25

Phyrophosphate is tolerable only when it is upto 10-fold of the Fe(III) concentration. Ammonium sulfate does not harm in the determination even when it is present about 700 times to Fe(III).

D I S C U S S I O N

Preliminary studies show that the procedure developed has a number of advantages. There is no effect of time on the intensity of color. Some cations and anions which interfere in the KCNS method have no effect in this determination. It is therefore instructive to compare the two methods. This is done in table. XI.

T A B L E XI

A COMPARISON OF THE THIOCYANATE AND THE FERROCYANIDE METHODS FOR Fe(III)

Properties	KCNS method	Ferrocyanide method
1. Sensitivity	0.01 μg	0.1 μg
2. Stability of color	Fades rapidly unless stabilized	stable for at least 5 hours
3. pH-range	0 - 1.5	0 - 2.5
4. Effect of excess reagent	increase in intensity	None

T A B L E XI
(Continued)

Properties	KCNS method	Ferrocyanide method
5. Beer's law	slight deviation	obeyed
6. Interference of cations	Ag^{+}, Hg^{+}, Cu^{+2}, Bi^{+3}, Ti^{+4}, U^{+6}, Mo^{+6} and Osmium	(a) Hg^{+} does not interfere (b) Ag^{+}, Cu^{+2}, Mo^{+6} and Os tolerable upto equal concentration with Fe (c) Bi^{+3}, Ti^{+4} and U^{+6} tolerable upto 10-fold (d) Cd^{+2} and Zn^{+2} interfere
7. Interference of anions	Fluoride, pyrophosphate, Oxalate, sulfate and phosphate	(a) Fluoride, oxalate, sulfate and phosphate do not interfere (b) Pyrophosphate is tolerable upto 10-fold (c) Chromate, dichromate, thiosulfate, sulfide and permanganate interfere.

Since a number of complexing anions i.e. tartrate, fluoride and citrate do not effect the determination of iron by potassium cyanide-potassium ferrocyanide reagent, it is possible that many other interferences may be removed by the selection of a proper complexing agent and the proper pH.

It has not been possible to study the mechanism of the color developed. It is probably due to the fact that a few CN^- ions enter the coordination sphere of iron and hence the prussian blue precipitate is not formed but a blue solution is obtained. The same effect was noticed when KCN was replaced by EDTA or sulfosalicylic acid. However, KCN was found to give the best results as far as the determination of iron was concerned for the following reasons:

(i) Potassium cyanide - potassium ferrocyanide reagent is stable for at least 48 hours since KCN inhibits the oxidation of ferrocyanide.

(ii) Sulfosalicylic acid - potassium ferrocyanide reagent develops a green color on standing overnight.

(iii) If 5% KCN in the reagent is replaced by 5% EDTA

precipitation occurs on the addition of buffer after some time. However, if 1% EDTA is taken then there is no precipitation but the color develops very slowly.

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C H A P T E R V

PREPARATION AND PROPERTIES OF STANNIC TUNGSTATE

The work in these laboratories was recently started on synthetic inorganic ion exchangers based on tin (1,2,3). These ion exchangers proved highly selective and a number of difficult and important separations were achieved on papers impregnated with stannic phosphate and stannic tungstate (2,3). A search of literature showed that no systematic work has been done on stannic tungstate. Lotz (4) prepared it first and studied its properties in a cursory manner. It was, therefore, decided to study its composition and properties. The present chapter summarizes the results of such a study.

E X P E R I M E N T A L

Reagents: Stannic chloride pentahydrate (Poland) and sodium tungstate (B.D.H. Analar) were used in these studies. All other reagents and chemicals were of reagent grade.

Apparatus used: Spectrophotometric studies were performed on Bausch and Lomb spectronic 20 colorimeter. pH measurements were made on mains operated pH-meter (Electronic and Industrial Instruments Co. Pvt. Ltd., Hyderabad, India) and high frequency titrations were performed on Sargent Oscillometer of type V (E.H. Sargent & Co., Chicago) in a 100 ml cell.

Preparation of Stannic Tungstate: Stannic tungstate gel was prepared by mixing aqueous solutions of 0.02M stannic chloride and 0.02M sodium tungstate in the (molar) ratio 2:1. It was digested at room temperature for several hours, washed with water, filtered and dried at room temperature. When the gel was immersed in water it broke

down easily to small particles with cracking and slight evolution of heat. For distribution studies the gel was broken down to the desired particle size in a porcelain mortar and sized by seiving. To convert it into the hydrogen form it was immersed in dilute KNO_3 for 24 hours, the acid being intermittantly replaced, it was then washed several times with water till the pH of the washing water was 6. Then it was filtered and dried in air.

R E S U L T S

1. Physical properties of Stannic Tungstate:

Stannic tungstate is in the form of white, hard and semitransparent grannules suitable for column operation. When the exchanger was placed in HCl it turned yellow. The change in color was not observed with H_2SO_4, KNO_3, $HClO_4$ or sodium chloride solutions.

2. Effect of heating on Stannic Tungstate:

When stannic tungstate was heated with water no change in color or form was observed. But on heating at higher temperature for one hour in a muffle furnace the color of the exchanger changed as given in table XII.

T A B L E XII

EFFECT OF HEATING ON STANNIC TUNGSTATE

Temperature	Color of the beads
100°C	White
200°C	White
300°C	Very light yellow
400°C	Light brown
500°C	Brown
600°C	Dark brown
700°C	Blackish brown
800°C	Blackish

3. Composition: 0.100 gm of the ion exchanger was dissolved in 50 ml of concentrated hydrochloric acid. The solution was diluted to 100 ml. Standard sodium molybdate solution (40 ml) containing 1000 ppm Mo was added to it. The mixture was then cooled to 5-10°C in an ice bath and the separation of tin from molybdenum along with tungsten was achieved by α-Benzoinoxime as usual (5). Molybdenum and tungsten were estimated as lead molybdate and lead

tungstate (6). The actual weight of tungsten was calculated by difference. Lead molybdate was added only because α-benzoinoxime does not precipitate tungsten completely if present alone (7). Tin in the filtrate was reduced with lead and sulfuric acid and determined both iodometrically and oxidometrically (8), the results in both cases were found to be the same. High frequency titrations were performed by taking 2.0 ml of 0.1M sodium tungstate solution in the cell and running 0.1M aqueous solution of stannic chloride from the burette. The results are shown in figure 9.

4. Ion Exchange Capacity: The jelly was found to be a cation exchanger. Its ion exchange capacity was, therefore, determined by taking uni- and bivalent metal ions using the standard method (9). The rate of flow of the effluent was kept 10-12 drops (app. 0.5-0.6 ml) per minute and the column was prepared in a burette of internal diameter 1 centimeter. The results are summarized in table XIII.

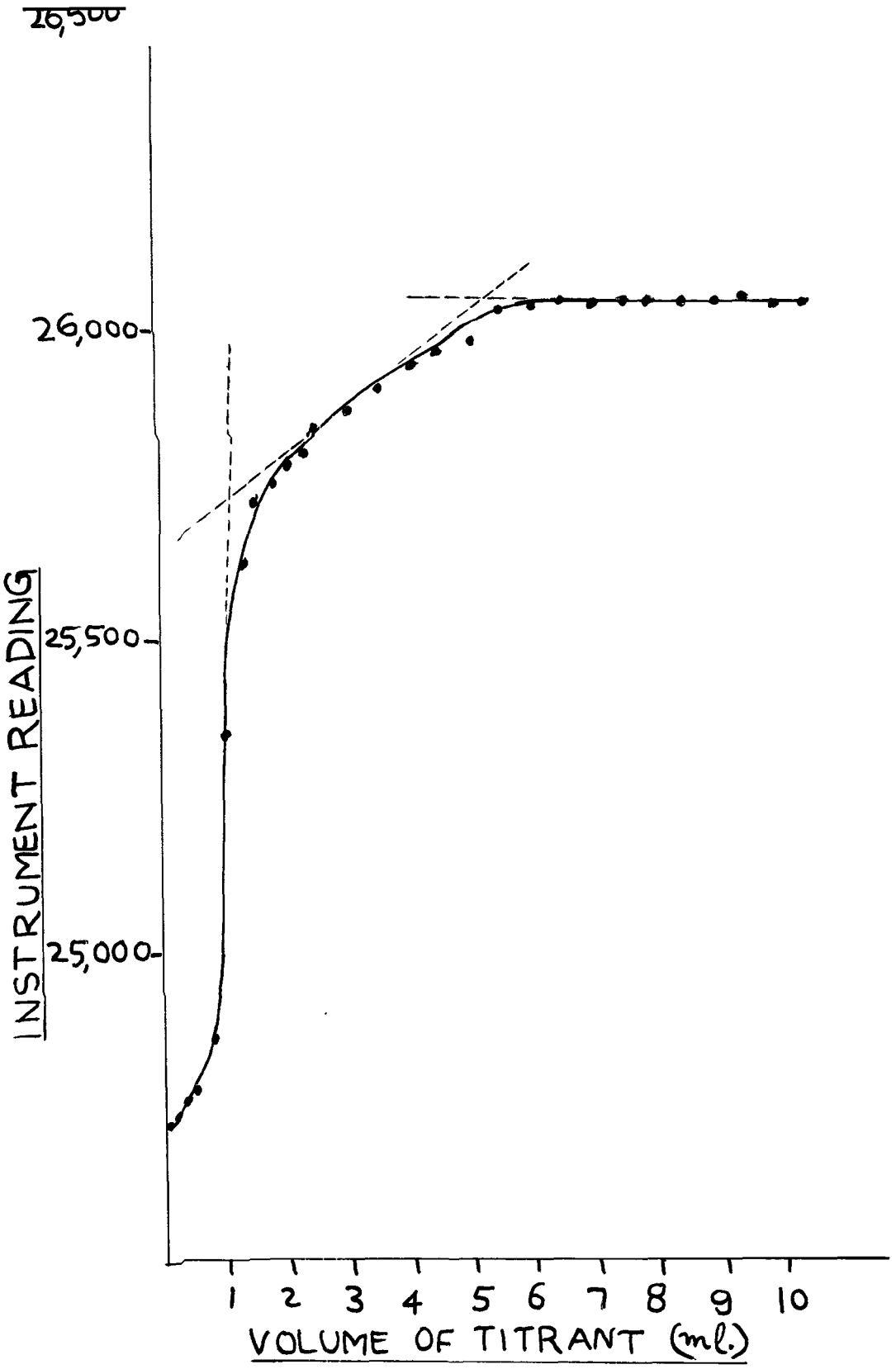


FIGURE - 9. HIGH FREQUENCY TITRATION OF SODIUM TUNGSTATE AGAINST STANNIC CHLORIDE.

T A B L E XIII

ION EXCHANGE CAPACITY OF STANNIC TUNGSTATE

Metal ion	Capacity (m.eq./gm dry exchanger)
Na^+	0.50
K^+	0.57
Mg^{+2}	0.58
Sr^{+2}	0.59

5. Chemical Stability: To test its chemical stability visually 0.2-0.5 gm of the dry ion exchanger was kept in 25 ml of hydrochloric acid, nitric acid, sulfuric acid, perchloric acid, formic acid, acetic acid and ammonia. Only in hydrochloric acid the color of the beads turned yellow within five minutes and in others the exchanger remained unaffected even after keeping for 48 hours. Detailed studies on the solubility of the ion exchanger for different solvent systems were performed as follows:

The exchanger was washed with hot water to remove any tin or tungsten remaining adsorbed on the beads after

the initial washing. 500 mg of the exchanger were then refluxed with 50 ml of the solution under study for 1 hour. After cooling the solution was filtered and in the filtrate tungsten was determined spectrophotometrically with thiocyanate and tin with phenylfluorone (10,11). Tin was determined in distilled water and 8M HNO_3 only because in these cases no tungsten was found dissolved which was confirmed quantitatively, and thus no prior separation of tin from tungsten was necessary. The results are summarized in table XIV.

T A B L E XIV

CHEMICAL STABILITY OF STANNIC TUNGSTATE

Solution	Amount of W (mg)	Amount of Sn (mg)
distilled water	0.00	0.065
16M HNO_3	7.25	-
8M HNO_3	0.00	0.27
4M HNO_3	0.00	-
4.5M H_2SO_4	22.50	-
2M H_2SO_4	7.75	-

T A B L E XIV
(Continued)

Solution	Amount of W (mg)	Amount of Sn (mg)
1M H_2SO_4	4.25	-
2.5M HCl	16.00	-
1M HCl	14.00	-
60% $HClO_4$	1.00	-
10% $HClO_4$	1.00	-
1M Oxalic acid	dissolved appreciably	
0.5M Oxalic acid	,,	,,
0.25M Oxalic acid	255.00	-
0.1M Oxalic acid	125.00	-
1M NH_4OH	320.00	-
0.5M NH_4OH	dissolved appreciably	
0.1M NH_4OH	45.00	
1M NaOH	dissolved completely	
0.1M NaOH	20.00	-
0.01M NaOH	20.00	-

6. pH-titration curve: For titration the following method was followed:

Several 250 ml conical flasks each containing one gram of the ion exchanger were taken and different milli-equivalents of sodium hydroxide (.1 to 1) were added keeping the volume in all cases constant (100 ml) by adding distilled water. The flasks were then shaken in an electric shaker at room temperature for 4 hours. After equilibrium the pH was recorded of all the solutions. The experiment was repeated in the presence of sodium chloride keeping sodium ion concentration constant (0.1M). The results are shown in figure 10.

7. Elution curve: To find out the maximum suitable concentration of KNO_3 (100 ml) for complete elution of hydrogen ion from the exchanger, different concentrations of KNO_3 solution were taken. The results are shown in figure 11. The elution curve was drawn by taking a 1M solution of KNO_3 (figure 12).

8. Distribution Coefficients: The utility of this ion exchanger for the separations of analytical interest was examined by determining the distribution coefficients for different metal ions in distilled water. The method followed was as below:

In a conical flask 0.5 ml of the cation solution and 49.5 ml of demineralized water were taken. The concentration of the cation was so adjusted that the amount of the cation does not exceed 3% of the total capacity of the exchanger taken (12). Then 0.5 gm of the exchanger in H^+ form (50-100 mesh) was added. The flask was placed at 25 $\pm$ 1°C for 6 hours in a constant temperature water bath with occasional shakings. Forty milliliters of the solution were then withdrawn from the flask and poured into a beaker and titrated against the standard EDTA solution by the standard methods (13). The results are summarized in table XV.

T A B L E XV

DISTRIBUTION COEFFICIENTS FOR METAL IONS ON STANNIC TUNGSTATE

Metal ion	Compound used	K_d
Pb^{+2}	nitrate	150.0
Mn^{+2}	sulfate	114.6
Zn^{+2}	nitrate	41.4
Mg^{+2}	nitrate	94.4
Cd^{+2}	acetate	77.8

T A B L E XV
(Continued)

Metal ion	Compound used	K_d
Cu^{+2}	nitrate	116.0
Ni^{+2}	sulfate	136.8
Co^{+2}	nitrate	586.0
Ba^{+2}	nitrate	156.0
Sr^{+2}	nitrate	114.0

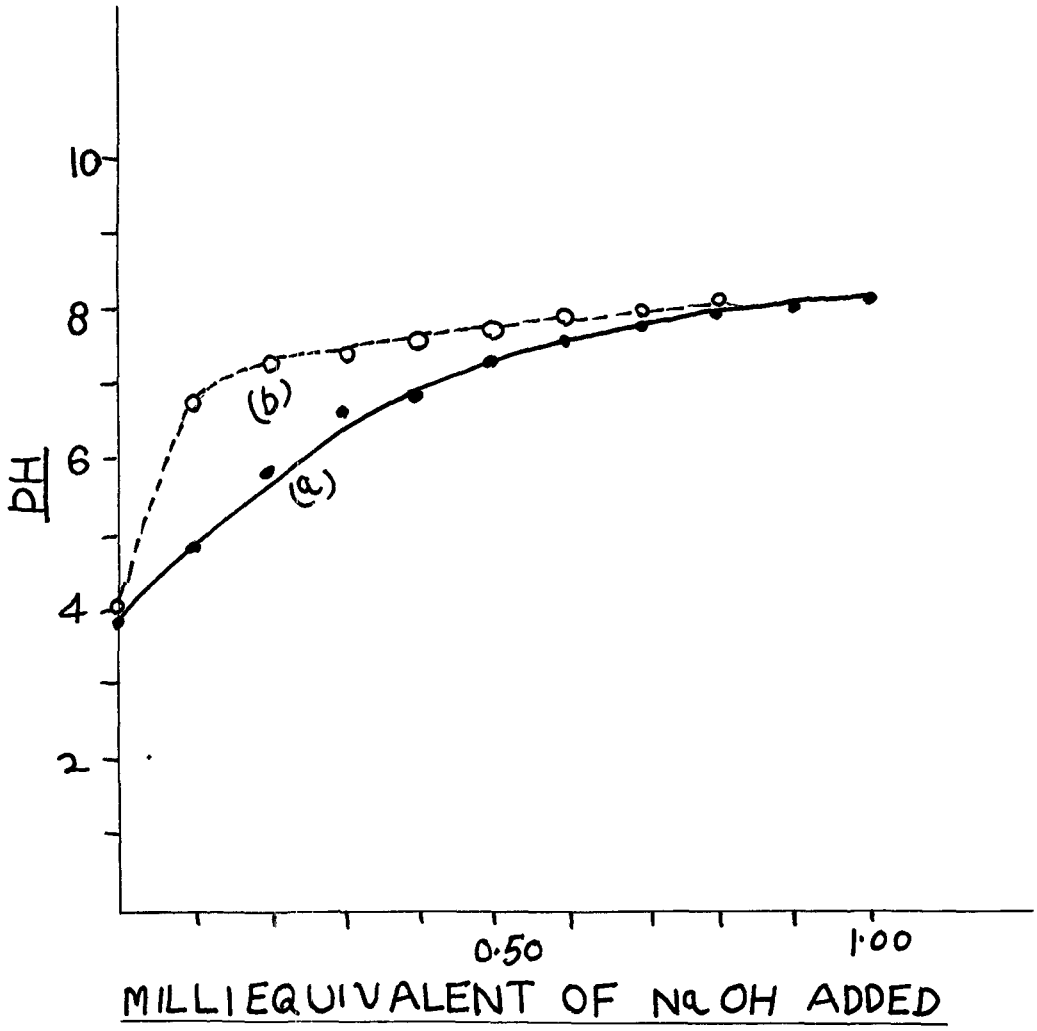


FIGURE - 10. pH-TITRATION CURVE FOR STANNIC TUNGSTATE
(a) IN THE ABSENCE OF NaCl
(b) IN THE PRESENCE OF NaCl

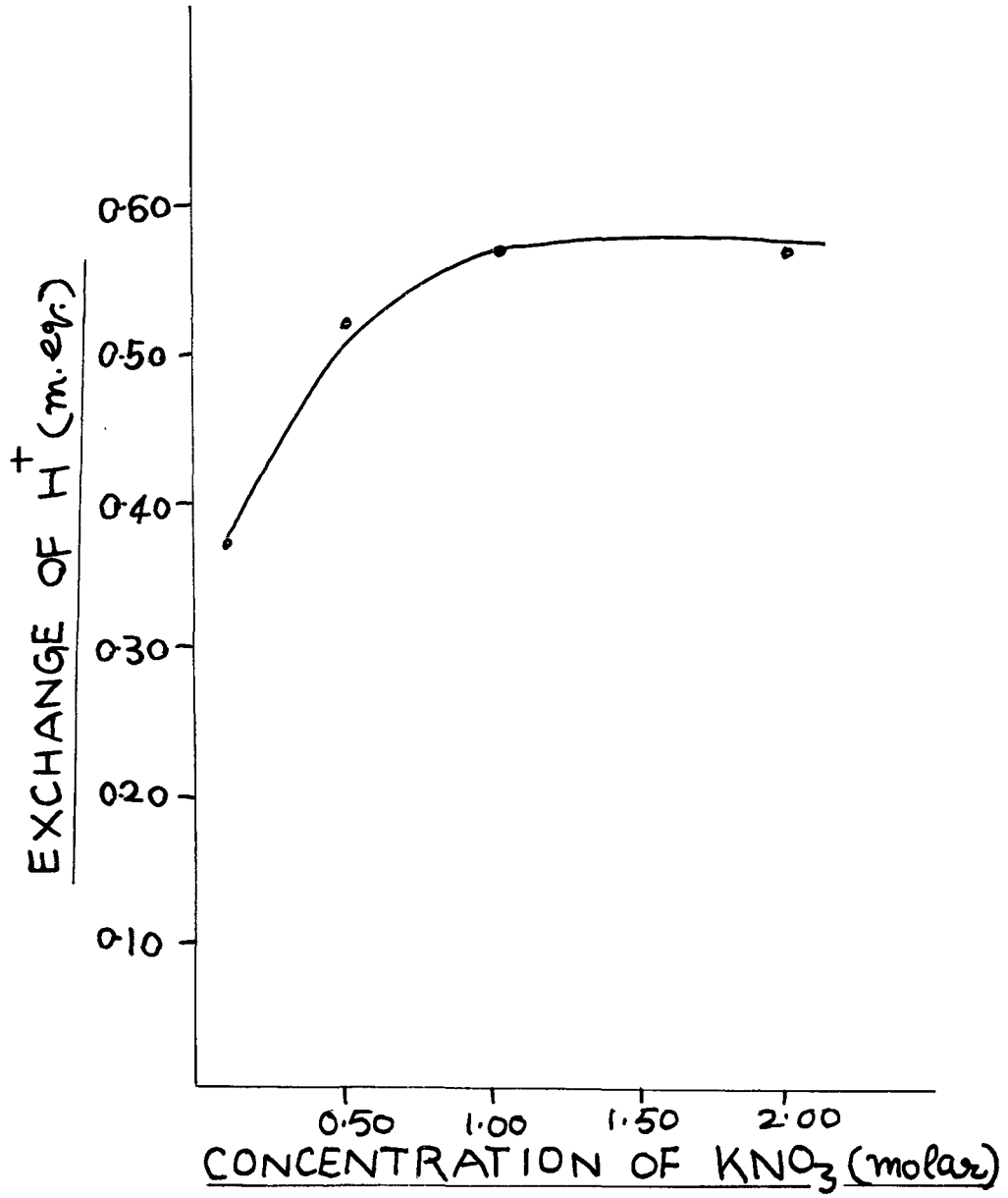


FIGURE - 11. EXCHANGE CAPACITY OF STANNIC TUNGSTATE AS A FUNCTION OF CONCENTRATION OF ELUENT.

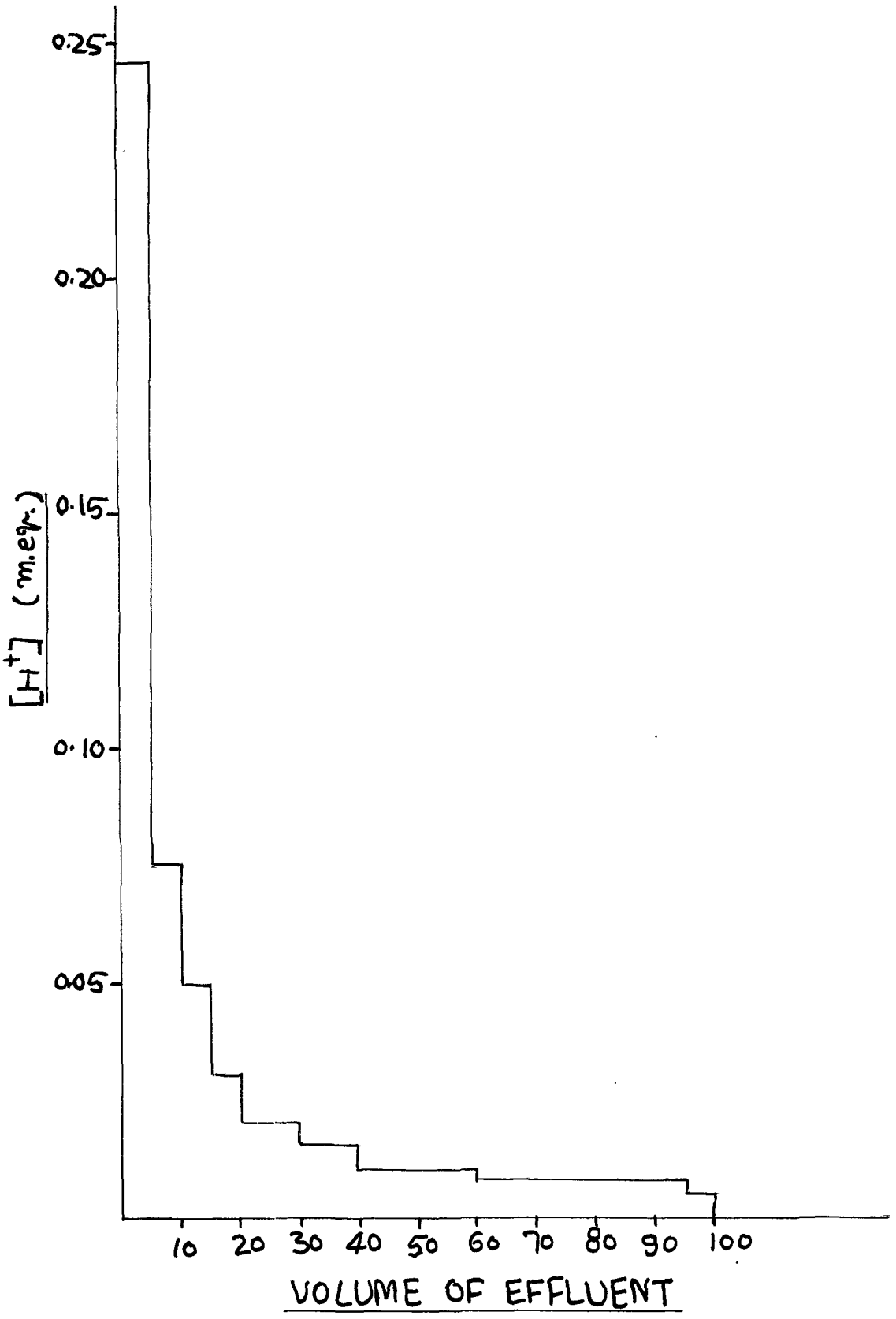


FIGURE - 12. ELUTION CURVE OF STANNIC TUNGSTATE.

D I S C U S S I O N

The observed K_d values show that stannic tungstate is a useful ion exchanger and many interesting separations are possible. This has been demonstrated by the paper chromatography of cations performed in these laboratories (1,3). Of the numerous successful separations achieved on paper some may be possible on ion exchange columns also (table XVI). The K_d values for Ba^{+2}, Sr^{+2} and Mg^{+2} are in the same order as for stannic molybdate (2) and zirconium phosphate (14). The Rf values of metal ions in 0.1M $HClO_4$ are also qualitative in agreement with the K_d values provided the ions belonging to the same group in the periodic table are considered (table XVI).

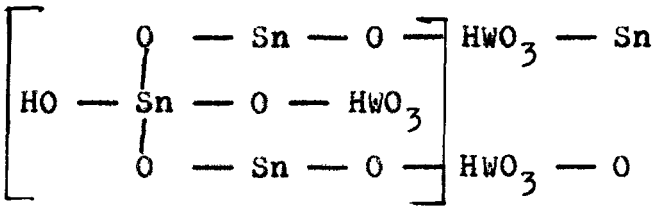
T A B L E XVI

COMPARISON OF K_d VALUES WITH R_f VALUES ON STANNIC TUNGSTATE PAPERS

S.No.	Cation	K_d	R_f in 0.1M $HClO_4$
1.	Pb^{+2}	150.0	0.07
2.	Mn^{+2}	114.6	0.23
3.	Zn^{+2}	41.4	0.53
4.	Mg^{+2}	94.4	0.75
5.	Cd^{+2}	77.8	0.58
6.	Ni^{+2}	116.0	0.87
7.	Cu^{+2}	136.8	0.55-0.00
8.	Co^{+2}	586.0	0.28
9.	Ba^{+2}	156.0	0.36
10.	Sr^{+2}	114.0	0.41

The composition of stannic tungstate was found to be Sn:W (3:1). The high frequency titrations confirm this conclusion. When stannic chloride is taken in the titration cell and titrated with sodium tungstate, no end point is obtained, since in this case the conductivity is very high owing to the low pH of the solution. However,

when sodium tungstate is taken in the cell two breaks are obtained corresponding to Sn:W (1:2) and Sn:W (3:1). The precipitate first formed corresponds to the normal stannic tungstate which changes on addition of more stannic chloride to the tungstate actually isolated. The structure of stannic tungstate may be tentatively postulated as follows: Since only one inflection point is observed in pH-titration curve, it appears that the exchanger behaves as a monofunctional acid:



Stannic tungstate does not give a yellow color with HNO_3 or with sodium chloride alone. However, when they are mixed a yellow color is observed showing that some complex formation with HCl occurs. This, however, needs further study. The pH-titration curves show that initially there is some hydrolysis (pH=4). Now on the addition of NaOH alone there is a slow increase in pH. However, when (NaCl + NaOH) is added there is a sharp initial increase in pH. This may be explained as follows: On the addition

of sodium hydroxide the change in pH is not considerable since some OH^- ions are adsorbed at the site of the exchanger. However, when a mixture of (NaCl + NaOH) is used there is a considerable excess of Cl^- ions which (9 : 1) replaces the OH^- ions and there is a sharp increase in the pH. For similar reasons the titration is much quicker in the presence of NaCl than in its absence [Cf figure 10, curves 'a' and 'b']. Figure 11 shows that capacity of stannic tungstate is strongly dependent on $[K^+]$ and it becomes constant at 1M $[K^+]$. The elution curve (figure 12) shows that almost all hydrogen ions are released in the first 25 ml of the eluent. Further elution replaces the hydrogen ions only to a small extent. In both these aspects the behaviour of stannic tungstate resembles closely to the behaviour of stannic molybdate. The ion exchange capacity of stannic tungstate is lower than that of stannic phosphate (15) and stannic molybdate (2). However, this disadvantage is compensated by the fact that stannic tungstate is much more stable than stannic molybdate table (XVII).

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ANALYTICAL CHEMISTRY

Allyl Alcohol as a Sensitive and Specific Reagent for the Detection of Mercurous Ions

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Allyl Alcohol as a Sensitive and Specific Reagent for the Detection of Mercurous Ions

SIR Very few sensitive and specific tests exist for the mercurous ion because of its weak complex-forming ability (*6*) The usual test with ammonia, though sensitive and specific, is not applicable in acidic and neutral media and it is also subject to interference from the precipitation of colored hydroxides Welcher *et al* (*7*) first proposed the use of allyl alcohol as a reagent for mercurous ions His method is specific but not sensitive which probably accounts for the fact that it has not gained wide acceptance In the course of our chromatographic studies (*3*) we independently noted that a spot of mercurous ion when exposed to allyl alcohol turned black Since no detailed studies have been recorded on this test we decided to investigate it further As a result we have been able to devise a very sensitive and specific test for mercurous ions

EXPERIMENTAL

Reagents. Reagent grade or double distilled solvents were used in this study Allyl alcohol (E Merck, Darmstadt) gave a positive test for aldehyde It was refluxed over solid potassium carbonate and distilled (*5*) Mercurous nitrate solution was prepared according to Kolthoff and Larson (*2*) The purity of mercurous nitrate solution was tested by the method of Kolthoff (*1*) Schleicher and Schull 2043a paper was used in these studies

Procedure To one drop (0 05 ml approximately) of the slightly acidic test solution is added a drop of 0 1*M* $AgNO_3$ and a drop of pure allyl alcohol A black precipitate or coloration shows the presence of Hg_2^{+2}

RESULTS

Reaction Studies. Preliminary studies (*4*) had indicated that out of about 200 organic substances only a few unsaturated compounds give a black precipitate with mercurous nitrate at room temperature Efforts were therefore made to compare the sensitivity of these reagents for the detection of mercurous ions

A drop (0 05 ml approximately) of the pure liquid was mixed with a drop of $Hg_2(NO_3)_2$ solutions of different concentrations—e g , 0 1*M*, 0 01*M*, 0 001*M*, etc Ascorbic acid was used in the solid state (1 mg approximately) The colors were noted within two minutes Ammonia was also included for comparison The results are summarized in Table I

Table I. Sensitivities of Different Organic Substances for Mercurous Ions

Substance	Sensitivity, μg
Allyl alcohol	12 5 (33, on paper)
Acetoacetic ester	50
Acetyl acetone	62 5
Ascorbic acid	25
Ammonia	9 (25, on paper)

Since allyl alcohol was found to be the most sensitive reagent for mercurous ions, it was decided to investigate the specificity and sensitivity of this reaction in the presence of other cations In these studies comparison was also done with ammonia

REACTION OF DIFFERENT CATIONS AND ANIONS WITH ALLYL ALCOHOL AND AMMONIA

CATIONS A spot of 0.1 *M* solution of the cation concerned was applied to the paper followed by a spot of allyl alcohol or ammonia as required. Most cations were used as nitrates. Only As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}, and Ti^{+3} were used as chlorides and Cu^{+2}, Fe^{+2}, and Fe^{+3} as sulfates. Mercurous ion was used both as nitrate and perchlorate. Of a large number of cations tested using allyl alcohol, only mercurous ion gave a positive test (either as a nitrate or perchlorate salt). Cations giving no color with the reagent are Ag^{+}, Cu^{+2}, Pb^{+2}, Hg^{+2}, Bi^{+3}, Cd^{+2}, As^{+3}, Sb^{+3}, Ni^{+2}, Co^{+2}, Ba^{+2}, Sr^{+2}, Ca^{+2}, Mg^{+2}, Tl^{+3}, U^{+4}, V^{+5}, Be^{+2}, Sn^{+2}, Al^{+3}, Cr^{+3}, Fe^{+2}, Fe^{+3}, Mn^{+2}, Zn^{+2}, Mo^{+4}, Ti^{+3}, Th^{+4}, Zr^{+4}, La^{+3}, Ce^{+4}, K^{+}, Na^{+}, and Pd^{+2}. Several of the cations giving a negative test with allyl alcohol did yield brown to black precipitates or spots with ammonia—i.e., Ag^{+}, Co^{+2}, V^{+5}, Fe^{+2}, Fe^{+3}, Mn^{+2}, and Mo^{+4}.

ANIONS A spot of the 0.1 *M* solution of the anion concerned was applied to the paper followed by a spot of allyl alcohol. All the anions were used as the sodium salts. No change in color was obtained in any case.

DETECTION OF MERCUROUS ION IN PRESENCE OF OTHER CATIONS

Interference Studies CATIONS. The 0.1 *M* solutions of mercurous nitrate and the nitrate of other cations were mixed in specified ratios. One drop of the solution was mixed with a drop of allyl alcohol (app. 0.05 ml.) on a spot plate. The results are summarized in Table II.

A mixture was also prepared by taking 0.1 ml. of the 0.1 *M* solutions of nitrates of each of the following cations Ag^{+}, Hg_2^{+2}, Pb^{+2}, Bi^{+3}, Cd^{+2}, Cr^{+3}, Ba^{+2}, Fe^{+3}. A drop of this test solution was mixed with a drop of allyl alcohol. An immediate black coloration was obtained showing the presence of Hg_2^{+2}.

ANIONS. A drop (approximately 0.05 ml.) of 0.1 *M* $Hg_2(NO_3)_2$ solution was mixed with a drop of 0.1 *M* solution of the anion concerned in the form of sodium salt followed by a drop of allyl alcohol or concentrated aqueous ammonia solution as required. Of a large number of common anions studied only iodide and phosphate interfered with development of the black precipitate. However a positive test can still be obtained for mercurous ions.

Mechanism of the Reaction Qualitative tests indicate that the product of mercurous nitrate–allyl alcohol reaction is pure mercury. This reaction can be explained in two ways: either mercurous nitrate oxidizes allyl alcohol first to an aldehyde then to an acid (Equation 1) or mercurous nitrate is decomposed catalytically by allyl alcohol according to Equation 2.

$$Hg_2^{+2} + CH_2{=}CH{-}CH_2OH \rightarrow 2Hg + 2H^{+} + CH_2{=}CH{-}CHO$$

$$Hg_2^{+2} + CH_2{=}CH{-}CHO + H_2O \rightarrow 2Hg + 2H^{+} + CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}OH \qquad (1)$$

$$Hg_2(NO_3)_2 \rightarrow Hg + Hg(NO_3)_2 \qquad (2)$$

The latter mechanism has been suggested by Zappi and Manini (*8*). However our observations do not entirely agree with this point of view. The reaction mixture containing mercurous nitrate and allyl alcohol gave negative tests for aldehyde, using the nitroprusside, Schiff's reagent and 2,4-dinitrophenyl hydrazine. However, formation of acid in the reaction mixture was shown by titration with alkali, after first removing mercurous ions with excess sodium chloride. This can be easily explained if it is presumed that mercurous nitrate oxidizes a part of allyl alcohol to an acid (Equation 1). We also noted that a small quantity of allyl alcohol reduced a large quantity of mercurous nitrate if the precipitated mercury was continuously removed. It is therefore probable that the reduction of mercurous nitrate to mercury proceed through both mechanisms.

DISCUSSION

Allyl alcohol offers a sensitive and specific test for the detection of mercurous ions. The method is most sensitive if the mercurous nitrate solution is 0.01 *M* in nitric acid. Higher acidity somewhat decreases the sensitivity of the allyl alcohol test. Cations other than Hg_2^{+2} seem to increase the sensitivity of the allyl alcohol reaction probably because these ions promote the reduction of mercurous to mercury. In the presence of excess phosphate or excess iodide the allyl alcohol and ammonia tests for mercurous ions fail. A positive test is obtained if the mixture is treated with excess silver nitrate (if iodide is present) or zirconium nitrate (if phosphate is present). The addition of excess of silver nitrate or zirconium nitrate results in the formation of stable yellowish white silver iodide or zirconium phosphate and thus releases mercurous ions. If now allyl alcohol is added, a black precipitate is obtained due to the reduction of the mercurous ions.

Table II. Sensitivity of Allyl Alcohol Reaction in Presence of Other Cations

Cation present	Allyl alcohol: Limit of detection, μg	Allyl alcohol: Dilution	Ammonia: Limit of detection μg	Ammonia: Dilution
Ag^{+}	0.008	1 60 000	5	1 100
Pb^{+2}	0.5	1 1,000	50	1 10
Co^{+2}	0.5	1 10 000	50	1 10
Cr^{+3}	0.5	1 1 000	5000	1 1
Bi^{+3}	0.5	1 1 000	50	1 10

ACKNOWLEDGMENT

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Selective Determination of Iron by Potassium Cyanide–Potassium Ferrocyanide Reagent

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A NUMBER of methods are available for the determination of iron The thiocyanate method is probably the simplest and the phenanthroline procedure the best Recently (*1*) an effort was made to reduce the number of interferences in the phenanthroline method Ferrocyanide has been proposed as a reagent for the determination of iron (*2, 3*) However, the colloidal dispersion of ferric ferrocyanide was used and large amounts of ammonium sulfate interfered (*4*) An effort has therefore been made to develop a fast and selective procedure for the determination of Fe(III) This procedure is based on the solubility of ferrocyanide in potassium cyanide

EXPERIMENTAL

All the spectrophotometric studies were performed on a Bausch & Lomb Spectronic 20 colorimeter

Reagents and Chemicals. A standard iron solution containing 1000 ppm Fe was prepared from B D H Analar ferric ammonium sulfate in 1% v/v sulfuric acid This solution was diluted as needed with 1% v/v sulfuric acid

All other reagents and chemicals used were either E Merck (Darmstadt, Germany) grade or B D H Analar

The potassium cyanide–potassium ferrocyanide reagents consisted of a 1 1 1 mixture of aqueous 5% w/v potassium cyanide, 5% w/v potassium ferrocyanide in 0 2% aqueous sodium carbonate, and glacial acetic acid

A buffer solution of pH 1 42 was prepared by adding 200 ml of 1*N* sodium acetate to 240 ml of 1*N* HCl and diluting to 1 liter

PROCEDURE

In Absence of Impurities. To the solution containing 5–50 μg of Fe(III) in 1% H_2SO_4, add 0 2 ml of 5% KCN, 0 2 ml of the coloring reagent, and 5 ml of buffer With distilled water make up to a 10-ml volume and measure the absorbance at 710 mμ

In Presence of Ba, Sr, and Hg(I). If a precipitate appears after the addition of the KCN, centrifuge After removal of the precipitate, proceed as described above

In Presence of Th(IV) and Y(III). To the solution in 1% H_2SO_4, add NaF solution (about 2000 μg fluoride), and proceed as above

In Presence of NO_2^- and Tl(I). If NO_2^- is present, heat the mixture with 1% H_2SO_4 for 15 minutes before adding KCN Cool and proceed as above Interference from Tl(I) can be removed by heating the mixture with a few drops of concentrated HNO_3

In Presence of Zr(IV) and Sb(III). To the mixture add sodium tartrate (2000 μg tartrate) Proceed as above When Sb(III) is taken as antimony tartrate it does not interfere in the procedure

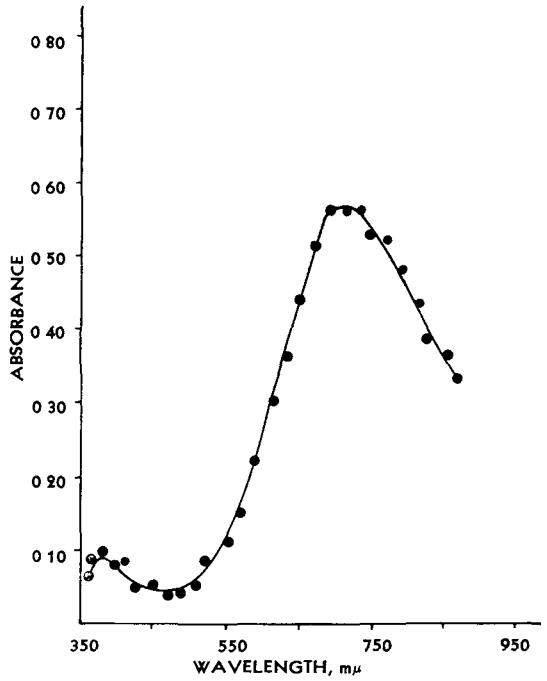

Figure 1 Absorption spectrum of blue color

RESULTS

The absorption spectrum of the color measured against the blank is shown in Figure 1

Measurement of the color at various time intervals showed that there was no change in absorbance for 5 hours

Varying the temperature from room temperature up to 80° C and measuring the absorbance showed that there was no effect up to 40° C Thereafter, there was a decrease of about 0 25 absorbance unit per 10° C up to 80° C

Measurement of the color at different pH values gave the results shown in Figure 2

Varying the amount of KCN in the procedure showed that the color intensity decreases with increases in the amount of KCN Excesses of the color reagent had no effect on the intensity of the color

The calibration curve prepared by following the procedure with varying amounts of Fe(III) showed that the Beer-Lambert law was valid between 5 to 50 μg of Fe(III) Absorbance at 5 μg Fe(III) was 0 077, at 50 μg, it was 0 71. The standard deviations were 0 0025 and 0 005, respectively

Effect of Diverse Ions. CATIONS The maximum amounts of cations in μg tolerable with 20 μg Fe(III) are given below Cr(III), 2080, Pt(IV), 2000, Se(VI), 2242, Mg, 2000, Te (VI), 12761, Al(III), 2698, Ca, 2000, Hg(I), 10030, Sr, 2000, Ba, 1377 Th(IV) 2320, Pb(II), 10360, Sb(III), 2030, W(VI), 18386, Pd(II), 1064, Zr(IV), 2030, Tl(I), 2320, Be (II), 903, Sn(II), 147, Sn(IV), 295, Bi(III), 209, U(VI), 250, Ti(IV), 252, As(III), 749, Mo(VI), 120, Co(II), 147, V(IV), 128, Mn(II), 28, Ni(II), 25, Cu(II), 64, Ag(I), 22, Os, 25.

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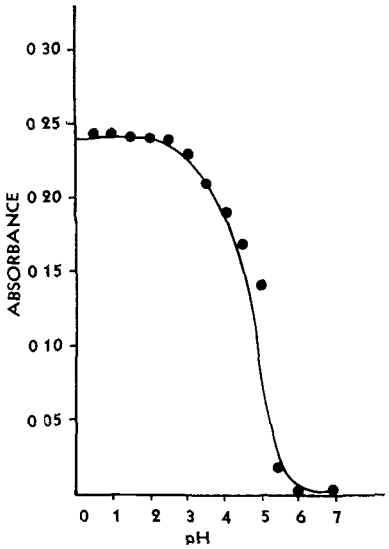

Figure 2. Effect of pH on blue color

ANIONS To the Fe(III) solution the anion under study was added and the Fe(III) determined Of 20 anions studied, most were noninterfering even at 100-fold concentrations The amounts shown below are the maximum tolerable amounts with 20 μg of Fe(III) formate, 2250, iodide, 2540, bromide, 2000, citrate, 2080, chlorate, 2088, oxalate, 2200, iodate, 2050, bromate, 2560, arsenate 2317, arsenite, 5940, nitrite, 2000, tartrate, 2000, sulfite, 2000, fluoride, 2090, phosphate, 2376, hydrogen phosphate, 2380 Pyrophosphate is tolerable only up to 10-fold of Fe(III) concentration

DISCUSSION

The thiocyanate and ferrocyanide methods for Fe(III) are compared in Table I

Since a number of complexing anions do not affect this iron determination, it is possible that other interferences might be removed by the selection of a suitable complexing agent and pH This, however, needs further study

The explanation of the color developed has not been studied However, it is probably caused by the fact that a few CN ions enter the coordination sphere of iron and hence the prussian blue precipitate is not formed but a blue solution is obtained The same effect was noticed when KCN was replaced by EDTA or sulfosalicylic acid However, KCN gave the best results for the following reasons The KCN–ferrocyanide reagent is stable for at least 48 hours, KCN inhibits the oxidation of ferrocyanide The sulfosalicylic acid–ferrocyanide reagent develops a green color on standing overnight If 5% KCN in the reagent is replaced by 5% EDTA, precipitation occurs on the addition of buffer (after some time) However, if 1% EDTA is used, there is no precipitation, but color development is slow

Table I Comparison of Thiocyanate and Ferrocyanide Methods for Fe(III)

Properties	KCNS method	Ferrocyanide method
Sensitivity	0 01 μg	0 1 μg
Stability of color	Fades rapidly unless stabilized	Stable
pH range	0–1 5	0–2 5
Effect of excess reagent	Increasing sensitivity	None
Beer's law	Slight deviation	Obeyed
Interferences of cations	Ag(I), Hg(I), Cu(II), Bi(III), Ti, U, Mo, Os	Hg(I) does not interfere, Ag(I), Cu(II), Mo, Os tolerable to equal with Fe concn , Bi(III), Ti(VI), U(VI) tolerable to 10-fold, Cd(II), Zn (II) interfere
Interferences of anions	Fluoride, pyrophosphate, oxalate, sulfate, phosphate	Fluoride, oxalate, sulfate, phosphate do not interfere, pyrophosphate is tolerable to 10-fold, chromate, dichromate, thiosulfate, sulfide, permanganate interfere

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